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Investingation and Chemisorption study of Oxygen Atoms and Cr (100) surface by DFT calculation

A.Kazemi Babaheydari[1], K. Zare[2,*] and F. Mollaamin[3]

[1]Ph. D Student, Science and Research Branch, Islamic Azad University, Tehran,Iran
[2]Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran,Iran
[3]Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran

ABSTRACT

This study concerns about quantum chemical modeling behavior of O_2 on Cr (100) surface by using density functional theory (DFT) by LANL2DZ and $6-31G^*$ basis sets. we presented the results of our first principles electronic structure calculations on the O2 molecules and their interface with Cr (100) surface. The chromium metal has the body-centered cubic structure, and chromium cluster has five Cr atoms that used to form the perfect Cr (100) surface. Three possible adsorption site, top, bridge and center site are considered in the calculations. The predicted results show that the bridge site are considerably stronger than at top and center site. So the bridge site approach is important for the chemisorptions processes, because the adsorption energy is lower than top site.

Keyword: DFT; Chemisorption;Surface;Cr(100);O2 molecule.

INTRODUCTION

Reactivity of elemental metal surface is under study both experimentally and computationally for many metals [1].The motivation for such studies is the fundamental in sight on the reactivity and chemical properties of such surface[1]. So experimental and theoretical studies of chemisorptions on vicinal surface are of great current in terest due to close connection coreal catalytic substerest [2]. The adsorption of gases on metals surface studied in the past year. so adsorption of CO on Cr_2O_3 has been the subiect of several experimental studies in the past 15 year[3].or oxidation of pure CU(100) has been studied both simolationally [4] and experimentally [5] by menay people.

Recently a large amount of experimental and theoretical work was reported on the characterization of chromium and chromium oxide G. M. Tonetto, M. L. Ferreira , D. E. Damiani study A combined theoretical and experimental study of NO decomposition on Pd and Pd-Mo catalysts [6] or Wen. Kaichen and jun. qianli [7] study of O_2 adsorption and dissociation on $CuCr_2O_4$ (100) surface and Masahiro Katoh and Manabu Shinkaw study

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*.Corresponding author : K.Zare

adsorption properties of gases on mesorporous chromium silicate[8].

The techniques most frequently applied were Low-energy electron diffraction (LEED) [9, 10] angular resolved ultraviolet photoelectron spectroscopy (ARUSP) [9, 10] and infrared spectroscopy [11-15].

In this work we preparation of chromium and present a theoretical electronic and geometry studies adsorption of O_2 on Cr (100) surface. For studies and calculation of adsorption we used Density Functional Theory (DFT) approaches method. The purpose of our present effort is to undertake DFT calculations for oxygen adsorption for the Cr (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 METHOD

The path of density functional theory (DFT) begun when Hohenberg and Kohn suggested in 1964 that the many –body wave function was al together too complicated an entity to be dealt with according to the methods of the variational principle.

Metals and metal oxide surface are a very interesting challenge for chemists and physicist they play an important role for catalysis of many industrial processes as well as in car combustion[16].

They theorized and later, in their work [17] , proved that another , much simpler entity can be chosen for the basic variable: the electron density which minimizes the total energy. This means that the ground state of the system is defined by that electron distribution.They zlso proved that all other ground state properties of the system (lattice constant, etc) can be calculated as functionals of the ground state density. Shortly following in 1965, Mer- min [18] extended the Hohenberg- kohn arguments to the finite temperature canonical and grand canonical ensembles. They are not widely used, but this illuminates the generality of density functional theory. The fact that all properties of any system are defined by it's ground state density ni (r) means that one scalar function , dependent only of the position r, defines all the information in the many – body wavefunctions for the ground state and all the excited states. As mentioned, all other properties of matter can then be calculated as functional of the ground state electron density (in mathematics , a functional is defined as a function that takes a set functions as it's basis). The original works by Hohenberg and kohn and of mermin [18] that state the priif of the existence of such functional do nit, however, offer any means how to cinstruct them. Thus The whole Density Functional Theory would thus remain nothing more but theoretical curiosity, if it was not for the kohn – sham ansatz, which provides a way to construct approximate ground state functional for real systems of many electrons [19].

Now, as the basic idea of the Density functional Theory is introduced, let us state the fundamental theorems behind the theory lies are originally stated and proven in the work of the Hohenbereg and kohn in 1964, as mentioned earlier.

This establishes the desired result and thus concudes the proof. [20]

In this paper is devoted to the study of the interaction of O2 molecule with the Cr (100) surface.

All the theoretical results present in this paper were obtained by means of quantum chemical embedded cluster calculation. The electronic structure of the system O2/Cr (100) is described by function based density functional theory (DFT) method; it is well known that the generalized gradient approximation (GGA) is needed to give an accurate description of energetic of bulk Cr phases and the cluster fragment is considered as a doublet molecules with partitioning of the basis sets for O atoms described by the standard 6- 31G* basis set. But for chromium the standard LANL2DZ basis set is used.

Chromium has the body – centered cubic structure with a lattice constant of $2.88\,A^{\circ}$ and every metal layer contains five Cr atoms as shown in fig .1. The O_2 molecule one per unit cell is allowed to approach the Cr (100) surface along three different symmetrical sites: 1- Directly on top of a Cr atom (top site) 2- on the middle of two nearest neighbor Cr atom (bride site) 3- in the center of the smallest unit structures of the surface (center site). For geometry optimization, the computations are performed with the Gaussian 98 package.

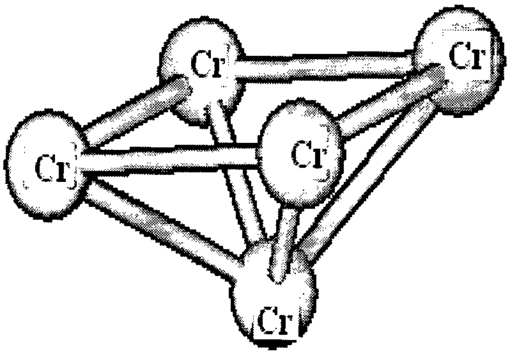

Fig. 1. The body-centered cubic structure of Cr with a Miller plane (100).

RESULTS AND DISCUSSION

In this paper study a slap approach is adopted to describe the metallic surface the structure of the clean Cr(100) surface is shown in (Fig .1) and the distance between the metals is $2.88\,A^{\circ}$. we consider O_2 molecules in unit cells that contain five Cr atoms. O_2 adsorption on the clean surface of chromium was followed for Cr(100) surface . Whean O_2 molecule is allowed to approach the Cr(100) surface along three different symmetrical sites. The various configurations discussed in this paper could be present at the surface of a Cr(100) sample in equilibrium with the O_2 gas phase .

In this study, we have carried out the calculation for intereaction of the adsorption O_2 molecules with Cr (100) surface so the adsorption energy of the O_2 molecules is computed as:

$$E_{ads}= E\,(O_2/Cr) - (E\,(O_2) + E\,(Cr\ surface))$$

In equation the first term is the total energy of the O_2/Cr surface super molecule and second and third terms are total energy of separated fragments.

We start by describing the O_2 chemisorption process at different site on Cr-surfac.there are three high symmetry site on chromium surface, consider first site of top site (Fig. 2).

In the vertical top site(fig. 2a) O_2 molecules is allowed to approach the chromium surface in different distance and their chemissorption energy are calculated with P/LANL2DZ , 6-31G* basis sets . The first optimized chemisorpton distance (Rd) that for O_2/ Cr (100) surface for vertical top site is $1.8\,A^{\circ}$ and chemisorption energy is – 164/62 ev. In the next step chemisorption in distance of is calculated with increase of the distance between the oxygen and oxygen atoms. In this state the optimized R(o=o)is $1.41\,A^{\circ}$ and calculated energy of chemisorption in this state(Table1).

In the horizontal top site(fig. 2b) O_2 molecules is allowed to approach the chromium surface in different distance and their chemisorptions energy are calculated with P/LANL2DZ , 6-31G* basis sets . The first optimized chemisorptions distance (Rd) for O_2/ Cr(100)surface for horizontal top site is $1.85\ A^{\circ}$ and chemisorptions energy is – 132/353ev . In the next step chemisorptions in distance of is calculated with increase of the distance between the oxygen and oxygen atoms. In this state the optimized R (O=O) is $1.41\,A^{\circ}$ and calculated energy of chemisorptions in this state that -132/3538ev (Table2)

For the vertical bridge site (fig.3a), O_2 molecule is allowed to approach the Cr(100) surface in different distance; so the optimized chemisorption distance (Rd) is $1.20\,A^{\circ}$ and chemisorptions energy is – 209/025ev while distance between the oxygen atoms is

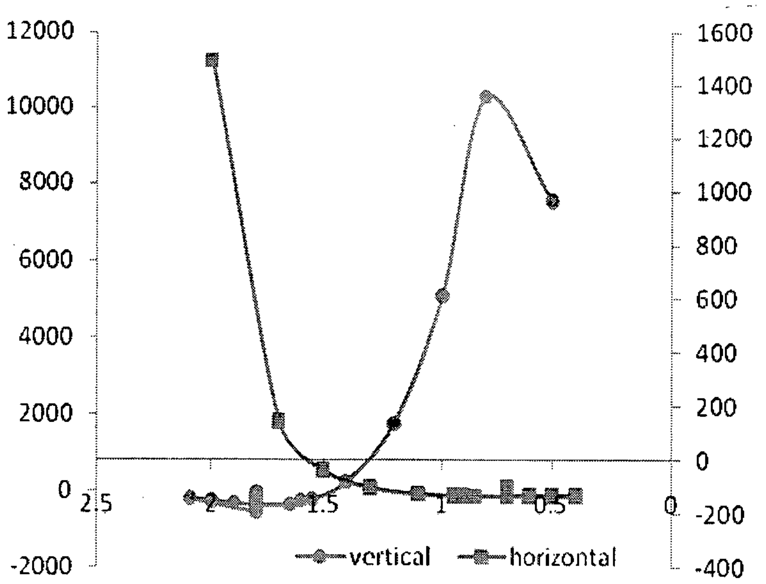

Fig. 2. High symmetry of O_2 adsorption vertical and horizontal top sites on Cr(100).

1.21 A$^{\circ}$ (table 3). In the next step chemisorptions in distance of is calculated with increase of the distance between the oxygen and oxygen atoms. In this state the optimized R(O=O)is 1.41 A$^{\circ}$ and calculated energy of chemisorptions in this state(table3).

For the horizontal bridge site (Fig.3b), O_2 molecule is allowed to approach the Cr(100) surface in different distance; so the optimized chemisorptions distance (Rd) is 1.20 A$^{\circ}$ and chemisorptions energy is – 170/044ev while distance between the oxygen atoms is 1.21 A$^{\circ}$ (table 4). In the next step chemisorptions in distance of is calculated with increase of the distance between the oxygen and oxygen atoms. In this state the optimized R(O=O)is 1.41 A$^{\circ}$ and calculated energy of chemisorptions in this state(table4).

In general chemisorption s at the bridge site are considerably stronger than at the top site.

This result is related to the fact that O2 are relatively much closer to the top site. for bridge site approaches O2 are closer to the Cr(100) surface (Rd=1.2 A$^{\circ}$) than that of the top site (Rd= 1.8 A$^{\circ}$) and the chemisorption energy is lower than top site.

In the vertical center site study (fig.4a) to O_2 molecule is allowed to approach on chromium surface different distance , thus optimized chemisorptions distance and calculated chemisorption energy are 0.70 A and -109.45 ev respectivety.In next step chemisorption energy in distance of 0.7A is calculated with increase of the distance between the oxygen atoms (R(O=O), Fig.4) . In this state the optimized R(O=O)is 1.51 A$^{\circ}$ and calculated energy of chemisorptions in this state that -114ev(Tables 5,6).

In general chemisorption s at the bridge site are considerably stronger than at the top site. This result is related to the fact that O_2 are relatively much closer to the top site. for bridge site approaches O2 are closer to the Cr(100) surface (Rd=1.2 A$^{\circ}$) than that of the top site (Rd= 1.8 A$^{\circ}$) and the chemisorption energy is lower than top site.

In the vertical center site study (fig.4a) to O_2 molecule is allowed to approach on chromium surface different distance , thus optimized chemisorptions distance and calculated chemisorption energy are 0.70 A and -109.45 ev respectivety.In next step chemisorption energy in distance of 0.7A is calculated with increase of the distance between the oxygen atoms (R(O=O), Fig.4) . In this state the optimized R(O=O)is 1.51 A° and calculated energy of chemisorptions in this state that -114ev(Tables 5,6).

Table 1 . Optimized parameter of Adsorption of O2 on Cr(100) at the P/LANL2DZ, ,6-31G*for Vertical Top Site

Vertical Top Site			
$R_d^a(A^o)$	$R(0=0)(A^o)$	E^b (ev)	E^c_{ads} (ev)
0.5	1.21	-93832.1664	965.5018
0.8	1.21	-93832.1664	1356.5019
1	1.21	-93832.1664	611.7436
1.2	1.21	-93832.1664	138.4681
1.4	1.21	-93832.1664	-78.3288
1.55	1.21	-93832.1664	-143.4481
1.6	1.21	-93832.1664	-147.0177
1.65	1.21	-93832.1664	-161.3552
1.8	1.21	-93832.1664	-164.6215
1.9	1.21	-93832.1664	-158.4484
2	1.21	-93832.1664	-149.1385
2.1	1.21	-93832.1664	-139.0042
1.8	1.41	-93832.1664	-191.2635
1.8	1.61	-93832.1664	-187.3875
1.8	1.81	-93832.1664	-171.5271
1.8	2.01	-93832.1664	-145.7641
1.8	2.21	-93832.1664	-139.2766
1.8	2.41	-93832.1664	-129.0972
1.8	2.61	-93832.1664	-117.5887
0.5	1.41	-93832.1664	2512.4638
0.8	1.41	-93832.1664	810.3399
1	1.41	-93832.1664	328.0471
1.3	1.41	-93832.1664	-47.4276
1.6	1.41	-93832.1664	-184.8823
1.8	1.41	-93832.1664	-191.2635
2.1	1.41	-93832.1664	-162.4244
2.4	1.41	-93832.1664	-27.1064
2.7	1.41	-93832.1664	-100.6247
3	1.41	-93832.1664	-85.7058

a. Distances of oxygen from the Chromium surface.

b.Adsorption energy O2 on Cr(100) surface at P/LANL2DZ,6-31G*.

c.Eads=E(O2/Cr(100)-EO2-ECr(100)

Table 2 . Optimized parameter of Adsorption of O2 on Cr(100) at the P/LANL2DZ, ,6-31G*for Horizontal Top Site

Horizontal Top Site

$R_d^a(A^o)$	$R(0=0)(A^o)$	E^b (ev)	E^c_{ads} (ev)
0.5	1.21	-93832.1664	11251.5674
0.8	1.21	-93832.1664	1801.1777
1	1.21	-93832.1664	544.9174
1.2	1.21	-93832.1664	89.9392
1.4	1.21	-93832.1664	-68.4173
1.6	1.21	-93832.1664	-116.0156
1.8	1.21	-93832.1664	-121.8091
1.85	1.21	-93832.1664	-132.3538
1.9	1.21	-93832.1664	-122.1091
2	1.21	-93832.1664	-120.9092
2.1	1.21	-93832.1664	-119.0395
2.2	1.21	-93832.1664	-117.1623
1.85	1.41	-93832.1664	-132.3538
1.85	1.516	-93832.1664	-130.2402
1.85	1.61	-93832.1664	-124.1074
1.85	1.81	-93832.1664	-115.9872
1.85	2.01	-93832.1664	-108.1891
1.85	2.21	-93832.1664	100.9934
1.85	2.41	-93832.1664	-93.4236
0.5	1.41	-93832.1664	11169.0191
0.8	1.41	-93832.1664	1738.2252
1	1.41	-93832.1664	501.4205
1.2	1.41	-93832.1664	67.69
1.4	1.41	-93832.1664	-83.3831
1.6	1.41	-93832.1664	-132.3788
1.85	1.41	-93832.1664	-132.3727
2	1.41	-93832.1664	-121.9056
2.3	1.41	-93832.1664	-98.4329
2.6	1.41	-93832.1664	-83.641
3	1.41	-93832.1664	-75.5894

a. Distances of oxygen from the Chromium surface.
b.Adsorption energy O2 on Cr(100) surface at P/LANL2DZ,6-31G*.
c.Eads=E(O2/Cr(100)-EO2-ECr(100)

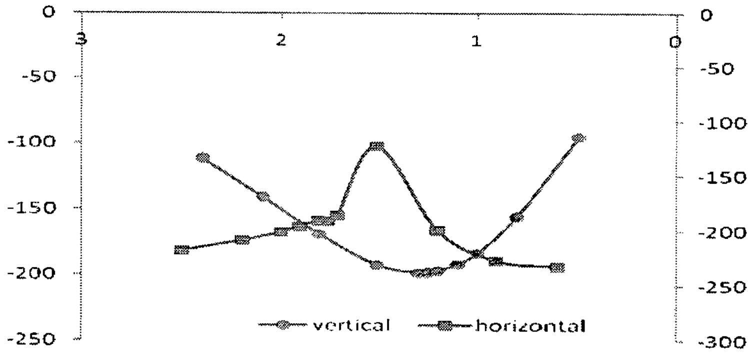

Fig. 3. High symmetry of O_2 adsorption vertical and horizontal bridge sites on Cr(100).

Table 3 . Optimized parameter of Adsorption of O2 on Cr(100) at the P/LANL2DZ, ,6-31G*for Vertical bridge Site

Vertical bridge Site			
$R_d^a(A^o)$	$R(0=0)(A^o)$	E^b (ev)	E^c_{ads} (ev)
0.5	1.21	-93832.1664	-67.4579
0.8	1.21	-93832.1664	-154.8099
1	1.21	-93832.1664	-192.4472
1.1	1.21	-93832.1664	-203.2902
1.2	1.21	-93832.1664	-209.025
1.4	1.21	-93832.1664	-207.465
1.21	1.31	-93832.1664	-229.666
1.21	1.41	-93832.1664	-235.6817
1.21	1.71	-93832.1664	-229.3098
1.21	1.81	-93832.1664	-211.9305
1.21	2.01	-93832.1664	-220.6184
1.21	2.5	-93832.1664	-216.4171
0.5	1.41	-93832.1664	-114.5665
0.8	1.41	-93832.1664	-187.2566
1	1.41	-93832.1664	-220.5749
1.1	1.41	-93832.1664	-230.6388
1.2	1.41	-93832.1664	-236.3036
1.25	1.41	-93832.1664	-237.61
1.3	1.41	-93832.1664	-237.9588
1.5	1.41	-93832.1664	-231.3298
1.8	1.41	-93832.1664	-202.8039
2.1	1.41	-93832.1664	-169.0314
2.4	1.41	-93832.1664	-133.9144

a. Distances of oxygen from the Chromium surface.
b.Adsorption energy O2 on Cr(100) surface at P/LANL2DZ,6-31G*.
c.Eads=E(O2/Cr(100)-EO2-ECr(100)

Table 4 . Optimized parameter of Adsorption of O2 on Cr(100) at the P/LANL2DZ, ,6-31G*for Horizontal bridge Site

Horizontal bridge Site			
$R_d^a(A^o)$	$R(0=0)(A^o)$	E^b (ev)	E^c_{ads} (ev)
0.5	1.21	-93832.1664	-76.1583
0.8	1.21	-93832.1664	-141.2889
1.1	1.21	-93832.1664	-169.6698
1.2	1.21	-93832.1664	-170.0441
1.3	1.21	-93832.1664	-167.8137
1.5	1.21	-93832.1664	-154.2673
1.6	1.21	-93832.1664	-146.4158
1.8	1.21	-93832.1664	-130.7998
2	1.21	-93832.1664	-118.3223
1.2	1.31	-93832.1664	-187.7203
1.2	1.41	-93832.1664	-193.8385
1.2	1.61	-93832.1664	-190.6224
1.2	1.81	-93832.1664	-181.8325
1.2	2.01	-93832.1664	-173.7871
1.2	2.21	-93832.1664	-167.6477
1.2	2.41	-93832.1664	-163.2288
1.2	2.7	-93832.1664	-159.1244
1.2	3	-93832.1664	-159.6213

Table 4. Continued

1.2	3.3	-93832.1664	-155.0688
0.5	1.41	-93832.1664	-102.2332
0.8	1.41	-93832.1664	-166.1945
1	1.41	-93832.1664	-189.522
1.1	1.41	-93832.1664	-193.7483
1.2	1.41	-93832.1664	-193.7483
1.5	1.41	-93832.1664	-175.4034
1.8	1.41	-93832.1664	-145.7475
2	1.41	-93832.1664	-124.4144
2.3	1.41	-93832.1664	-96.2053
2.8	1.41	-93832.1664	-80.8862
2.9	1.41	-93832.1664	-75.0924
3.2	1.41	-93832.1664	-73.4288

a. Distances of oxygen from the Chromium surface.
b.Adsorption energy O2 on Cr(100) surface at P/LANL2DZ,6-31G*.
c.Eads=E(O2/Cr(100)-EO2-ECr(100)

Table 5 . Optimized parameter of Adsorption of O2 on Cr(100) at the P/LANL2DZ, ,6-31G*for Vertical Center Site

Vertical center Site			
$R_d^a(A^o)$	$R(0=0)(A^o)$	E^b (ev)	E_{ads}^c (ev)
0.5	1.21	-93832.1664	-87.4961
0.65	1.21	-93832.1664	-88.9711
0.7	1.21	-93832.1664	-109.4561
0.75	1.21	-93832.1664	-104.1993
0.9	1.21	-93832.1664	-78.2795
1	1.21	-93832.1664	-73.396
0.7	1.51	-93832.1664	-114.659
0.7	1.61	-93832.1664	-113.2738
0.7	1.81	-93832.1664	-113.2738
0.7	2.01	-93832.1664	-102.5224
0.7	2.21	-93832.1664	-73.396
0.7	2.41	-93832.1664	-52.4669
0.7	2.761	-93832.1664	-44.2732
0.7	3	-93832.1664	-41.4757
0.5	1.41	-93832.1664	-121.6369
0.65	1.41	-93832.1664	-121.18849
0.7	1.41	-93832.1664	-123.6152
0.75	1.41	-93832.1664	-122.8991
0.9	1.41	-93832.1664	-122.6367
1	1.41	-93832.1664	-115.2588
1.2	1.41	-93832.1664	-108.5512

a. Distances of oxygen from the Chromium surface.
b.Adsorption energy O2 on Cr(100) surface at P/LANL2DZ,6-31G*.
c.Eads=E(O2/Cr(100)-EO2-ECr(100)

Table 6 :. Optimized parameter of Adsorption of O2 on Cr (100) at the P/LANL2DZ, ,6-31G*for Horizontal Center Site

Horizontal Center Site			
$R_d^a(A^o)$	$R(0=0)(A^o)$	E^b(ev)	E^c_{ads} (ev)
0.45	1.51	-93832.1664	-221.2156
0.55	1.51	-93832.1664	-223.8707
0.65	1.51	-93832.1664	-222.8327
0.75	1.51	-93832.1664	-219.175
0.9	1.51	-93832.1664	-210.2325
1	1.51	-93832.1664	-203.8647
1.2	1.51	-93832.1664	-189.6979
1.4	1.51	-93832.1664	-172.3452
1.8	1.51	-93832.1664	-133.4288
2.2	1.51	-93832.1664	-92.8031
2.6	1.51	-93832.1664	-50.3413
0.55	1.31	-93832.1664	-215.6772
0.55	1.41	-93832.1664	-223.3482
0.55	1.61	-93832.1664	-220.8946
0.55	1.81	-93832.1664	-211.709
0.55	2.61	-93832.1664	-203.079
0.55	2.21	-93832.1664	-196.4224
0.55	2.41	-93832.1664	-191.5708
0.55	2.7	-93832.1664	-187.2664
0.55	3	-93832.1664	-184.6607

a. Distances of oxygen from the Chromium surface.
b.Adsorption energy O2 on Cr(100) surface at P/LANL2DZ,6-31G*.
c.Eads=E(O2/Cr(100)-EO2-ECr(100)

CONCLUSION

In summary, Density Functional Theory (DFT) begun when Hohenberg and Kohn suggested in 1964 that the many-body wave function was altogether too complicated an entity to be dealt with according to the method of the variational principle. The paper presents the results of quantum chemical calculations using Ab initio density functional theory method for adsorption of O2 molecules on Cr(100) surface with LANL2DZ and $6-31G^*$basis set. We can extract energetic information about the stability of adsorption O2 on Chromium surface and calculations adsorptions energy. The results obtained here used to interpret experimental data.

REFERENCES

[1] Pitkanen.Heikki, O and O2 Adsorpton on Ag/Cu(100) . (2005)

[2] F.Mollaamin , M.T.Baei, A. Kazemi Babaheydari journal of Physical & Theoretical Chemistry. 4 (2008) 229

[3] M.Pykavy , V. Staemmler , O.Seiferth, H. J. Freund, Surface Sci .479(2001)11-25

[4] puisto. Oxygen adsorption on clean and oxygen precovered Cu(100) , Masters thesis , lut, (2004)

[5] M . Hirsimaki. Private communication

[6] G.M.Tonetto , M.L.Ferreira , D.E. Damiani. Journal of Molecular. 193(2003) 121-137

[7] Xiang-Lan Xu , Wen-Kai Chen , Jun-qian Li . Journal of Molecular Structure: THEOCHEM. 860(2008)18-23

[8] Masahiro Katoh , Manabu Shinkawa , Tahei Tomida . journal of Colloid and Interface Science. 277 (2004) 280-284

[9] C.Xu , B.Dillmann , H . Kuhlenback , H.J. Freund. Phys. Rev.Lett. 67(1991)3551

[10] H . Kuhlenback , C.Xu , B.Dillmann, M.Hsbel , B. Adam , D. Ehrlich , S . Wohlrab, , H.J. Freund , U.A. Ditzinger, H.Neddermeyer, M.Neumann, Ber. Bunsenges. Phys.Chem. 96(1992) 15

[11] A.A.Davydov , Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides , Wiley, Chichester , New York , (1990).

[12] D. Scarano , G.Ricchiardi, S. Bordiga , P.Galletto, C. Lamberti, G. Spoto , A. Zecchina. Faraday . Disc . 105(1996)119

[13] M.I. Zaki, H.Knozinger, J.Catal. 119(1989)311

[14] K.Hadjiivanov, G.Busca . Langmuir . 10(1994)4534

[15] Z.ecchina , D. Scarano , , S. Bordiga , , G.Ricchiardi, G. Spoto ,F. Geobaldo . Catal. Today . 27(1996)403

[16] Wolfgang . Bergermayer . Ab-inito simulation of Atomic Adsorption on Vanadium Surface . Wien , Im Februar. (2002).

[17] P.Hohenberg, W.Kohn . Inhomogenous electron gas . Phys . Rev. 136(1964) B864-871

[18] N.D. Mermin, Thermal properties of the inhomogenous electron gas , Phys.Rev. 137(1965)A1441-1443.

[19] Richarad .M.martin. Electronic Structure Basic Theory and practical Methods. Cambridge university press, Cambridge.(2004)

[20] P.P.Rushton. Towards a Non-Local Density Functional ;Description of exchange and correlation . (2002)

[21] Jiang , D.E C Carter , E. A. Surf. Sci ;547, 85-98 (2003)

[22] W.Zhong , Y . Cai , D. Tomanek , Nature (London , United Kingdom) , 362 , 435,(1994).