Chemisorption of molecular oxygen on Cu(1 0 0): a Hartree–Fock and density functional study

J. Torras [a,b], C. Lacaze-Dufaure [a,c], N. Russo [a,*], J.M. Ricart [b]

[a] *Dipartimento di Chimica, Università della Calabria, I-87030, Arcavacata di Rende, Italy*
[b] *Departament de Química, Facultat de Química, Universitat Rovira i Virgili, Pça. Imperial Tàrraco 1, 43005 Tarragona, Spain*
[c] *CIRIMAT, Ecole Nationale Supérieure de Chimie de Toulouse, 118 route de Narbonne, 31077 Toulouse Cedex 4, France*

Abstract

The interaction of molecular oxygen with the Cu(1 0 0) surface has been studied by using both Hartree–Fock and density functional methods in the framework of the cluster model approach. In this study, we have used the $Cu_8(6,2)$ cluster in order to simulate the O_2 molecular adsorption on different high symmetry chemisorption sites (top–top, bridge–fourfold, bridge–top, fourfold–fourfold) on the Cu(1 0 0) surface. High level non-local density functional (NLSD) computations indicate that the more stable chemisorption site is the bridge–bridge followed by the top–top, bridge–top and bridge–fourfold ones. The calculated 1s O XPS shifts are in good agreement with the experimental indications. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chemisorption; Molecular oxygen; Density functional method

1. Introduction

The adsorption of molecular oxygen on a copper surface is a very important process related with many oxidation and catalytic reactions. A rich bibliography exits on this subject and is devoted to both experimental [1–6] and theoretical points of view [7–12].

Experimentally, the O_2-Cu(1 0 0) interaction has been investigated by using the near-edge X-ray absorption fine structure (NEXAFS) [1,2], surface-extended X-ray absorption fine structure (SEXAFS) [1,2], low energy electron diffraction (LEED) [2,3], thermal desorption spectroscopy (TDS) [2], ultraviolet photoelectron spectroscopy (UPS) [3], X-ray photoelectron spectroscopy (XPS) [3], high resolution electron loss spectroscopy (HREELS) [3,4] and scanning tunnelling microscopy (STM) [5,6]. These studies give some indications about the adsorbate species, but a complete structural, electronic and spectroscopic characterisation still not exists.

Some previous theoretical works have compared the O_2 chemisorption on Cu(1 0 0), Ni(1 0 0) and Pt(1 1 1) at a semi-empirical level of theory [7,8]. Fischer and Whitten [9] have made a preliminary study on the top–top dissociation of molecular oxygen on Cu(1 0 0) using a nine-atoms monolayer cluster and employing Hartree–Fock-configuration interaction (HF-CI) theory. A more complete dissociation path is given in the density functional work of Lou [10] in which mono-layer clusters of 4 and 6 copper atoms have been employed. Van Daelen et al. [11] also studied the reactivity of O_2 on Cu(1 0 0) at local and non-local density

* Corresponding author. Tel.: +39-984-492106;
fax: +39-984-492044.
E-mail address: nrusso@unical.it (N. Russo).

functional levels and considering as starting points the hollow–bridge, hollow–top and bridge–bridge molecular chemisorption sites. Finally, we mention the work of Gronbeck and Rosen [12] in which local spin density (LSD) computations have been performed considering a vertical O_2 approach on the on-top site on different Cu clusters.

This work follows our previous studies on the adsorption of atomic O on the (1 0 0) copper and silver surfaces [13–15] and is devoted to a preliminary study on the interaction of O_2 in different high symmetry chemisorption sites of the Cu(1 0 0) surface. Both Hartree–Fock (HF) and density functional (DF) levels of theory have been employed. In the initial stage of the work, we have explored several possibilities for the O_2/Cu(1 0 0) interaction using only the HF level of theory and considering different clusters ranging from $Cu_8(6,2)$ to $Cu_9(5,4)$ to $Cu_9(4,5)$. HF computations have revealed that the geometrical parameters and the binding energy for the similar chemisorption modes are almost the same using different cluster size. Subsequently, the computations have been redone at the DF level employing the $Cu_8(6,2)$ cluster that gives

the opportunity to study the different chemisorption sites on the same substrate.

2. Computational details

The results reported here have been obtained considering the highly symmetry chemisorption sites on Cu(1 0 0) surface simulated by the $Cu_8(6,2)$ cluster. In this cluster, there are six atoms in the first layer and two atoms in the second one. Following the previous indications [7–15], we have fixed the cluster geometry at the corresponding bulk data (Cu–Cu = 2.555 Å). The coordinates of the two oxygen atoms on the surface have been optimised imposing the constrain to respect the symmetry of the adsorption site (Fig. 1).

Ab initio Hartree–Fock SCF cluster wavefunctions have been obtained using the HONDO program [16]. In all the HF computations, the pseudo-potentials of Durand and co-workers [17,18] described the inner shells of Cu and the valence electrons ($d^{10}s^1$) of Cu have been described with a (3s, 3p, 4d/2s, 1p, 1d)
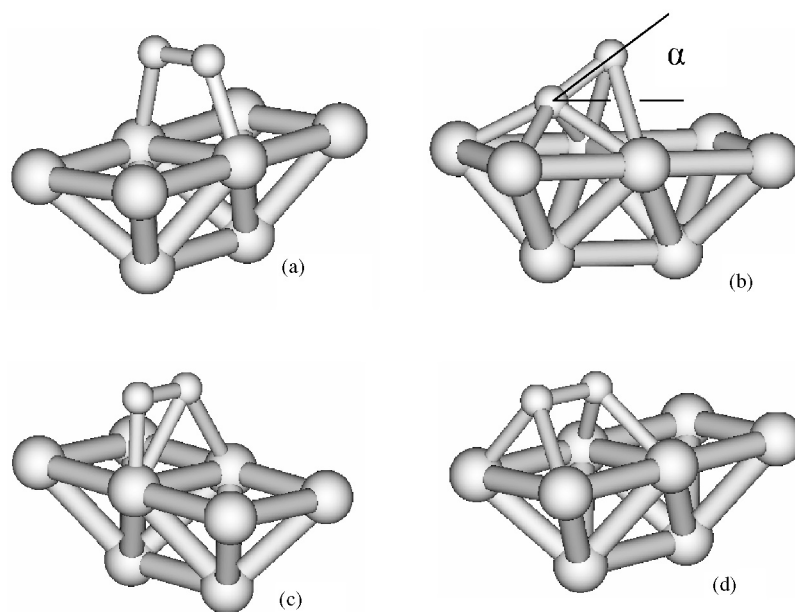

Fig. 1. Adsorption sites of O_2 over the Cu(1 0 0) surface simulated by the $Cu_8(6,2)$ cluster: (a) top–top site; (b) bridge–fourfold; (c) bridge–top; (d) bridge–bridge.

contracted GTO basis set. The all electron orbital basis set for oxygen was of the type (9s, 5p, 1d/4s, 3p, 1d).

DFT computations have been performed in the framework of the linear combination of gaussian type orbitals method implemented in the deMon package [19]. A relativistic (mass–velocity and Darwin terms) Cu^{+17} model core potential that allowed to treat explicitly the $3p^6 3d^{10} 4s^1$ Cu electrons has been employed in connection with a (3 1 1/3 1/3 1 1) orbital and (5,5; 5,5) auxiliary basis sets [20]. The all electron orbital basis set for oxygen was of triple zeta quality (7 1 1 1/4 1 1/1*) with the corresponding (4,4; 4,4) auxiliary one [21]. The optimisations have been performed by using the local VWN functional [22]. On the optimised structures, a single point computation has been done by using the exchange/correlation functionals proposed by Perdew and Wang [23] and Perdew [24], respectively (NLSD).

The binding energies (BE) have been obtained from the following expression:

$$BE = E(O_2/Cu_8) - (E(Cu_8) + E(O_2))$$

and using the triplet state energies for both O_2 and Cu_8 fragments.

3. Results and discussion

As mentioned in Section 1, we have firstly studied the O_2 interaction on different clusters and adsorption sites by using the HF method. From the results, we have concluded that the $Cu_8(6,2)$ cluster is a reliable model for study all the high symmetry chemisorption sites. Taking into account the same adsorption site, we have noted that the binding energy does not change significantly from one cluster to another (i.e. for the bridge–fourfold site, the obtained BE's values are 45

and 42 kcal/mol using $Cu_8(6,2)$ and $Cu_9(4,5)$ clusters, respectively).

In Table 1, the HF results for the more stable minima of the O_2 chemisorbed on $Cu_8(6,2)$ are presented. The bridge–fourfold adsorption site, in which one oxygen atom is in bridge position and the other in fourfold position (structure b in Fig. 1) appears to be the absolute minimum with a binding energy of 45 kcal/mol. The O–O computed distance is of 1.33 Å and the molecule lies almost parallel to the surface ($\alpha = 7°$). This distance is shorter than the SEXAFS experimental one (1.45 Å) [1,2], but it is larger than the HF calculated O–O distance for free O_2 (1.20 Å). The experimental counterpart for free O_2 is 1.21 Å [25]. This shows that the O_2 molecule and the Cu surface interact. The increased O–O distance can be attributed to a charge transfer of the metal substrate to the molecule, and to an increased population of the π^* levels of anti-bonding character, revealing a weakening of the intramolecular bond.

Concerning the Cu–O distance, we have found that $d_{O\perp Cu}$ of the two oxygen atoms (perpendicular distance between the oxygen and the surface plane) are 1.61 and 1.45 Å for the bridge and fourfold atoms respectively, while the corresponding experimental values are 1.55 and 0.88 Å [1,2]. Differences between experimental and theoretical results should be mainly attributed to three different facts. Firstly, we must consider the small cluster size used. It can affect the polarisation of the metal and introduce spurious frontier effects. Secondly, we use a symmetry constrained optimisation. The third reason is more important and concerns the electronic correlation effects that have not been taken into account. This lack affects both the geometrical parameters and the charge transfer and the partial ionic character of the interaction could not be correctly accounted. The introduction of cor-

Table 1
HF SCF optimised geometries of O_2 chemisorbed on different chemisorption sites over the Cu(1 0 0) surface simulated by the $Cu_8(6,2)$ cluster

Cluster	Chemisorption	BE (kcal/mol)	d_{O-O} (Å)	$d_{O1\perp Cu}$ (Å)	$d_{O2\perp Cu}$ (Å)	α (°)
$Cu_8(6,2)$	Fourfold–fourfold	32	1.30	1.68	1.68	0
	Top–top	38	1.30	1.85	1.85	0
	Bridge–fourfold	45	1.33	1.61	1.45	7
	Bridge–top	35	1.32	1.90	1.88	1
Experimental	Bridge–fourfold	–	1.45	1.55	0.88	27

relation effects is a necessary step. In any case, we can consider these computations useful essentially for choosing the appropriate cluster size.

Other than with the traditional post Hartree–Fock procedures (i.e. CI), the electronic correlation can be introduced with the more inexpensive density functional method. In the last decade, this tool has been widely used for study many electronic, geometrical and energetic parameters, especially for transition metal containing systems [26–28] including clusters [13,29–33]. We have redone the computations on O_2 adsorption on the $Cu_8(6,2)$ cluster optimising the geometries of the various O_2 chemisorption modes using the LSD approximation that gives reliable geometrical structures. In this step, we have removed the symmetry constrains. Furthermore, single point calculations on the LSD optimised geometries have been performed with the Perdew–Wang/Perdew gradient corrected exchange/correlation functionals in order to obtain more reliable binding energies. Results are collected in Table 2. We have considered both the $2S + 1 = 1$ and $2S + 1 = 3$ spin states for two reasons: firstly because the electronic state of the O_2/Cu_8 system was not known and secondly for the fact that the Cu_8 bare cluster has two spin states close each to other (we found at NLSD level that the Cu_8 singlet state is 11.2 kcal/mol more stable than the corresponding triplet one). The optimisation without the symmetry constrains indicates that the bridge–fourfold site with $2S + 1 = 3$ is not a real minimum on the potential energy surface but collapses in the bridge–bridge topology. At this point, we have also optimised the bridge–bridge adsorption mode considering the $2S + 1 = 1$ state. This last situation results as the more stable with a chemisorption energy of 30.6 kcal/mol. This result agrees with previous computations of Lou [10] and Van Daelen et al. [11], also performed at density functional level but with different clusters and exchange–correlation potentials. From Table 2, we can see that for the O_2/Cu_8 system, the two considered spin-states give very similar BE in all cases except for the bridge–bridge site. The bridge–fourfold site is the less stable with a BE value of 4.8 kcal/mol.

Comparison with Hartree–Fock results is difficult due to the different optimisation processes used but we underline that the binding energies computed at HF level are strongly overestimated with respect to these obtained with the DFT method for all the studied cases. Gradient-corrected BE indicate the bridge–bridge adsorption site as the preferred one. The experimental indications from NEXAFS and SEXAFS suggest the bridge–fourfold site as the most probable [1,2]. Other theoretical density functional results disagree with the experimental conclusion [10,11]. It is worth to note that EXAFS is not a technique able to give direct information on the geometrical parameters, but the topological indications coming from the experimental data need many physical approximations. In our study, agreement with experiment is found for the O_2 disposition on the bridge–fourfold adsorption site that in our computations is the unfavourable chemisorption site. We have found at DF level that the O_2 molecule is tilted by 31° (structure b in Fig. 1), in agreement with SEXAFS measurements ($\alpha = 27°$) [1].

In order to have further indications on the nature of the O_2-Cu(1 0 0) interaction, we have also calcu-

Table 2
DFT optimised geometries of O_2 chemisorbed on different chemisorption over the Cu(1 0 0) surface simulated by the $Cu_8(6,2)$ cluster[a]

Chemisorption	State	BE (kcal/mol)	$d_{O–O}$ (Å)	$d_{O1\perp Cu}$ (Å)	$d_{O2\perp Cu}$ (Å)	α (°)
Top–top	3	19.2	1.36	1.81	1.81	0
	1	19.5	1.35	1.77	1.77	0
Bridge–fourfold	3	–	–	–	–	–
	1	4.8	1.44	1.71	0.97	31
Bridge–top	3	12.4	1.40	1.79	1.81	−1
	1	14.6	1.34	1.79	1.75	−2
Bridge–bridge	3	23.1	1.43	1.47	1.43	−2
	1	30.6	1.43	1.44	1.44	0
Experimental	–	–	1.45	1.55	0.88	27

[a] Energies are computed at NLSD level, distances and angle come from LSD computations (see text).

lated the 1s O XPS shift at the NLSD level following the procedure previously described [32–34], on the preferred chemisorption site indicated by the experiments. The computed 1s O binding energy for the adsorbed oxygen molecule is 545.4 eV. The experimental XPS for the chemisorbed O_2 is 531.0 eV measured with respect to the Cu Fermi level [1,2]. Considering that the Fermi level is 4.59 eV [35], the difference between calculated and experimental 1s O core energies is of 9.9 eV. It is worth to note that the more important comparison is between the shifts with respect to the free adsorbate. For the O_2 free molecule, we find a BE of 553.2 eV for the quartet state (the corresponding experimental value is 543.1 eV). If we compare the shifts, we find 7.8 and 7.5 eV for the computed and the experimental one. The agreement with the experiment is good.

4. Conclusions

In this preliminary work, we have studied the interaction between O_2 and the Cu(1 0 0) surface using the HF and DFT methods and employing a Cu cluster with six Cu atoms in the surface layer and two in the second one, $Cu_8(6,2)$. HF computations have been performed essentially for the choice of the appropriate cluster. DFT results show that the preferred chemisorption site is the bridge–bridge one in disagreement with the experimental indication but in agreement with all previous high level theoretical computations. The 1s O XPS shift computed at the NLSD level for the bridge–fourfold site is in good agreement with the experimental counterpart.

Acknowledgements

References

[1] D. Arvanitis, T. Yokoyama, T. Lederer, G. Comelli, M. Tischer, K. Baberschke, Jpn. J. Appl. Phys. 32 (1992) 371.
[2] T. Yokoyama, D. Arvanitis, T. Lederer, M. Tischer, L. Tröger, K. Baberschkle, G. Comelli, Phys. Rev. B 48 (1993) 15405.
[3] A. Spitzer, H. Lüth, Surf. Sci. 118 (1982) 121.
[4] T. Sueyoshi, T. Sasaki, T. Iwasawa, Appl. Surf. Sci. 121 (1997) 562.
[5] P.J. Knight, S.M. Driver, D.P. Woodruff, J. Phys. Condens. Matter 9 (1997) 21.
[6] C. Cohen, A. Lhoir, J. Moulin, D. Schmaus, M. Sotto, J.L. Domange, J.C. Boulliard, Surf. Sci. 339 (1995) 41.
[7] B. Hellsing, S. Gao, Chem. Phys. Lett. 187 (1991) 137.
[8] B. Hellsing, S. Gao, Solid State Commun. 90 (1994) 223.
[9] C.R. Fischer, J.L. Whitten, Phys. Rev. B 40 (1989) 5745.
[10] L. Lou, Surf. Sci. 320 (1994) 320.
[11] M.A. Van Daelen, M. Neurock, R.A. Van Santen, Surf. Sci. 417 (1998) 247.
[12] H. Gronbeck, A. Rosen, Comput. Mat. Sci. 2 (1994) 607.
[13] J. Torras, J.M. Ricart, F. Illas, J. Rubio, Surf. Sci. 297 (1993) 57.
[14] J.M. Ricart, J. Torras, A. Clotet, J.E. Sueiras, Surf. Sci. 301 (1994) 89.
[15] J. Torras, M. Toscano, J.M. Ricart, N. Russo, J. Mol. Catal. A 119 (1997) 387.
[16] M. Dupuis, J. Rys, H.F. King, HONDO-76 program number 338 of QCPE, University of Indiana, Bloomington, IN 474001, USA, Pseudopotentials adapted by J.P. Daudey, M. Pélissier, General adaptation of ROHF methodology by R. Caballol, J.P. Daudey, CSOV adaptation by J. Rubio, F. Illas.
[17] P. Durand, J.C. Barthelat, Theor. Chim. Acta 38 (1975) 283.
[18] M. Pelissier, P. Durand, Theor. Chim. Acta 55 (1980) 43.
[19] A. St. Amant, Ph.D. Thesis, Université de Montreal, 1992.
[20] V. Musolino, N. Russo, M. Toscano, Phys. Lett. 165A (1992) 377.
[21] N. Godbout, D.R. Salahub, J. Andzelm, E. Wimmer, Can. J. Chem. 70 (1992) 560.
[22] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.
[23] J.P. Perdew, Y. Wang, Phys. Rev. B 33 (1986) 8800.
[24] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
[25] K.P. Huber, G. Herzberg, Constants of Diatomic Molecules, Van Nostrand, New York, 1979.
[26] J.M. Seminario (Ed.), Recent Developments and Applications of Modern Density Functional Theory, Elsevier, Amsterdam, 1996.
[27] C.W. Bauschlicher Jr., A. Ricca, H. Partridge, S.R. Langhoff, in: D.P. Chong (Ed.), Recent Advances in Density Functional Methods, Part II, World Scientific, Singapore, 1997.
[28] N. Russo, D.R. Salahub (Eds.), Metal–Ligand Interactions in Chemistry, Physics and Biology, NATO Science Series, Kluwer Academic Publishers, Dordrecht, 2000.
[29] C. Mijoule, M. Filali Baba, V. Russier, J. Mol. Catal. 83 (1993) 367.
[30] V. Russier, D.R. Salahub, C. Mijoule, Phys. Rev. B 42 (1990) 5046.
[31] P. Calaminici, A.M. Koster, N. Russo, D.R. Salahub, J. Chem. Phys. 105 (1996) 9546.
[32] L. Pedocchi, G. Rovida, N. Russo, J. Electron. Spectrosc. Relat. Phenom. 69 (1994) 81.
[33] L. Pedocchi, G. Rovida, N. Russo, Surf. Rev. 2 (1995) 563.
[34] L. Pedocchi, N. Russo, D.R. Salahub, Phys. Rev. B 47 (1993) 12992.
[35] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 74th Edition, CRC Press, Boca Raton, FL, 1993–1994.