

Dissociative Adsorption of Molecular Oxygen on the Cu(001) Surface: A Density Functional Theory Study

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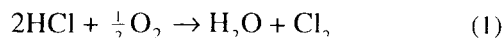
Abstract

The presence of atomic oxygen on catalytic surfaces is essential for initiating the oxidation of hydrogen chloride to produce chlorine via the so-called Deacon process. This process provides molecular chlorine for the formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) in combustion. In this paper, the dissociative adsorption of molecular oxygen on the Cu(001) surface has been studied using density functional theory. A periodic $p(3 \times 2)$ 4 layer slab was adopted to simulate the adsorption of both molecular and atomic oxygen at a number of adsorption sites. We have found that a bridge-bridge configuration is the most stable structure on Cu(001) with the O₂ molecule adsorbed horizontally. The activation barrier for the dissociative adsorption of O₂ resulting from this configuration was calculated to be 5.1 kcal/mol, with an equivalent transition temperature of ~66 K. This is in good agreement with the experimental value of 40 K obtained under ultra high vacuum conditions. We have also found that a less energetically favourable, vertically oriented, physisorbed structure leads to an almost negligible reaction barrier for the dissociative adsorption of O₂ on Cu(001) (1.5 kcal/mol), with an equivalent transition temperature of ~20 K.

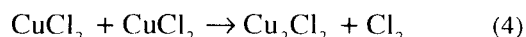
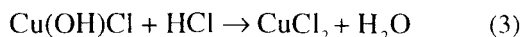
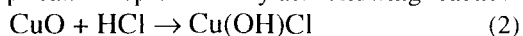
Keywords : DFT, Copper, Oxygen, Adsorption, Deacon reaction, Transition state

1. Introduction

Copper containing treatment agents (e.g., copper fungicides) aid the formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) in combustion processes. The predominant route for the formation of PCDD/F is the heterogeneous pathway, either through the burnoff of the carbon matrix or through catalysed condensation of gaseous precursors, especially phenols [1, 2]. These pathways involve chlorination steps via the so-called Deacon process [3], which entails the oxidation of HCl according to the following reaction:



where the presence of atomic oxygen is important for the completion of this reaction. Atomic oxygen, however, rarely occurs in the gas phase due to the high energy required to dissociate the oxygen molecule. As a result, the presence of a catalytic agent is generally required. Previous investigations show that copper and/or copper compounds are the preferable catalysts for this reaction [3-7]. The first step in the catalytic reaction mechanism is to provide the atomic oxygen necessary for oxidizing HCl. In the next step, the oxygen abstracts the hydrogen atom from the HCl to form copper chloride hydroxide (Cu(OH)Cl). The latter forms water leaving chlorine on the copper surface. These steps can be represented by the following reactions:



This paper investigates the dissociative adsorption of O₂ on the Cu(001) surface. We show that the geometry of the adsorbed molecule has a pronounced effect on the overall dissociative reaction mechanism. We show in particular that while horizontal configurations for an adsorbed O₂ molecule represent the most stable structures on Cu(001), a less stable vertical physisorbed structure presents an almost negligible reaction barrier for the dissociative adsorption of O₂ on Cu(001).

2. Methodology

All of the calculations have been performed within density functional theory (DFT) using the DMol³ code [8, 9]. A double-numeric quality basis set with polarisation functions (DNP) which is comparable to Gaussian 6-31G**, but more accurate than the Gaussian basis set of the same size [10], has been used to perform the calculations. All electrons have been treated for all atoms. The gradient corrected GGA functional for exchange and correlation has been employed [11], together with a Fermi smearing of 0.005 Ha and a real space cutoff of 4.4 Å.

The clean Cu(001) surface was modelled using a 4 layer slab and a $p(3 \times 2)$ supercell. The slab was repeated periodically in the x-y directions with a 1 nm vacuum region between the slabs in the z-direction. The Brillouin zone integrations were performed using the $4 \times 4 \times 1$ Monkhorst-Pack **k**-point sampling set [12]. The adsorption of oxygen

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was studied with the oxygen atoms and molecules adsorbed on the top layer of the slab. In all of the calculations the bottom two layers of the slab were kept fixed, while the remaining atoms in the top two layers and the adsorbed O atoms and/or molecules were allowed to move. The tolerances on the energy, gradient, and displacement convergence were set to 2×10^{-6} eV, 5×10^{-4} eV/Å, and 5×10^{-3} Å, respectively. The binding energies have been calculated using the formula

$$E_b = \frac{1}{n} [E_{O/slabb} - (E_{slabb} + nE_O)] \quad (5)$$

where E_{slabb} , E_O , and $E_{O/slabb}$ are the total energies of a clean slab, an isolated oxygen atom and the O/Cu (001) adsorption system, respectively. The binding energy E_b was thus calculated as an average over the n adsorbed oxygen atoms within each supercell.

Transition state searches have been performed using the synchronous transit methods [13]. These methods rely strongly on reasonable initial and final structures for the reaction system. Starting from optimised initial and final structures, the synchronous transit methods interpolate a reaction pathway to find a transition state. This is first done by performing a Linear Synchronous Transit (LST) followed by an energy minimisation in directions conjugate to the reaction pathway. A Quadratic Synchronous Transit (QST) maximisation is then performed to find the maximum energy structure along the reaction path to provide an upper limit to the barrier height for this reaction.

3. Results and Discussion

3.1 Bulk and Surface Properties

Adopting the methodology described above for bulk copper, the Cu lattice constant was found to be 3.672 Å. This is in good agreement with the experimental value of 3.615 Å [14] and the theoretical value of 3.67 Å determined by Fuchs *et al.* [15]. A periodic 4 layer slab for the clean Cu(001) surface was then constructed based on this calculated lattice constant, and the top two layers allowed to relax. The values for the calculated surface interlayer relaxations are listed in Table 1. The obtained results are seen to be in good agreement with both the experimental [16] and theoretical data [17].

Table 1: Calculated surface relaxations compared with theoretical and experimental data. Δd_{ij} is the relaxation between layers i and j .

	Δd_{12} (%)	Δd_{23} (%)
This work	-2.5	+0.70
Wang <i>et al.</i> [17]	-3.4	+1.5
Experiment [16]	-2.8	+1.1

3.2 Molecular Oxygen Adsorption

The adsorption of molecular oxygen on the Cu(001) surface has been studied by considering a

number of initial chemisorption sites. For horizontal O_2 adsorption, we have investigated four different sites – bridge-bridge, hollow-hollow, top-top and bridge-hollow (see Figure 1). The most stable adsorption site was found to be the bridge-bridge site with a 43.6 kcal/mol binding energy, followed by the top-top site with a binding energy of 23.9 kcal/mol. The hollow-hollow and bridge-hollow sites were found to be unstable with the O_2 molecule moving from these sites to the bridge-bridge site.

This latter result is in disagreement with experimental results which indicate that the most stable site for O_2 is the hollow-bridge site with the molecule oriented at 27° to the horizontal [18]. This is supported by Hartree Fock calculations by Torras *et al.* [19] which predicted that O_2 can be adsorbed at the bridge-hollow site with a 31° orientation to the horizontal. DFT calculations by Torras *et al.* [19], on the other hand, predicted that the bridge-bridge site is the most stable site for molecular oxygen adsorption. This is consistent with our results.

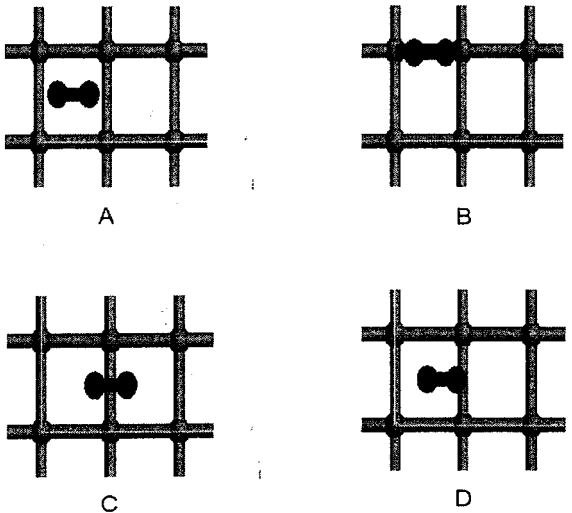


Figure 1: Different possible O_2 adsorption sites on the Cu(001) surface. (A) bridge-bridge, (B) top-top, (C) hollow-hollow, and (D) bridge-hollow.

The calculated parameters for molecular oxygen adsorption at a bridge-bridge site are summarised in Table 2. The results show that the O-O distance has increased by 23.7% to 1.51 Å from the O-O bond length in the gas phase which our calculations find to be 1.22 Å in excellent agreement with the measured value of 1.207 Å [20]. This value of 1.51 Å is a little longer than the SEXAFS results (1.45 Å) [21] and previous theoretical results (1.43 Å) [19]. The vertical distance between the surface and oxygen molecule is 1.35 Å, in agreement with other theoretical data [19]. We have also found that O_2 adsorption at the bridge-bridge site results in the interlayer relaxation between the first and the second layer being decreased from -2.7% for the clean surface to -0.27% for the adsorbed system. This change in the surface interlayer spacing is consistent with the charge transfer that occurs between the substrate and the molecule as evidenced by the significant increase in the O-O bondlength.

Table 2: Parameters of the O₂/Cu system. Horizontal adsorption at a bridge-bridge site.

Parameter	Value
O-O (Å)	1.51
Cu-O (Å)	1.98
⊥ Cu-O (Å)	1.34
Δd_{12} (%)	-0.27
Binding Energy (kcal/mol)	43.6

For the adsorption of molecular oxygen in a vertical configuration we have considered the high symmetry positions on the Cu(001) surface - the hollow, bridge and top sites. The most stable site for vertical molecular adsorption was found to be the hollow site with a binding energy of 14.5 kcal/mol. This was followed by the bridge site with a binding energy of 8.0 kcal/mol. The top site was found to be unstable, with the O₂ molecule moving from the top site to become adsorbed at a hollow site. The calculated parameters for molecular oxygen adsorbed above a hollow site are summarised in Table 3. The results show that the O-O distance has increased by 11.6% from the gas phase value of 1.22 Å to 1.362 Å, and the vertical distance between the surface and oxygen molecule is 1.16 Å. We have also found that the molecular adsorption of O₂ at this position does not change the distance between the first and second layers. This is consistent with this vertically oriented molecular configuration being physisorbed whereas the horizontally oriented O₂ molecule at the bridge-bridge site is chemisorbed.

Table 3: Parameters of the O₂/Cu system. Vertical adsorption at the hollow site.

Parameter	Value
O-O (Å)	1.36
Cu-O (Å)	2.20
⊥ Cu-O (Å)	1.16
Δd_{12} (%)	-2.5
Binding Energy (kcal/mol)	14.5

3.2 Reaction pathways

After finding the preferred sites for the attachment of molecular oxygen on Cu(001), the dissociation reaction pathways were explored via activation barrier calculations. Our calculations for the adsorption of atomic oxygen on Cu(001) have led us to conclude, in agreement with other calculations [22, 23], that the most stable site for atomic oxygen adsorption on Cu(001) is the hollow site. We have thus assumed that the dissociative state of the oxygen molecule on Cu(001) for both of our most stable horizontal and vertical adsorption structures corresponds to the two oxygen atoms being adsorbed on hollow sites. The optimized parameters corresponding to this latter configuration are presented in Table 4. It is interesting to note that

the vertical distance between each oxygen atom and the copper surface is found to be only 0.72 Å and that the calculated relaxation of the copper surface layer has changed from an inward relaxation for the clean surface of -2.7% to an outward relaxation of +0.54%.

Table 4: Parameters characterizing the adsorption of two O atoms on the Cu(001) surface at hollow sites.

Parameter	Value
Cu-O (Å)	1.94
⊥ Cu-O (Å)	0.72
Δd_{12} (%)	+0.54
Binding Energy (kcal/mol)	117.4

The calculated reaction pathway for the dissociative adsorption of O₂ starting from the horizontal bridge-bridge configuration is shown in Fig. 2, and the corresponding transition state parameters for this reaction pathway are presented in Table 5. The activation energy for this reaction has been calculated to be 5.1 kcal/mol. The equivalent temperature to this energy is around 66 K. This agrees well with the experimental data obtained under ultra high vacuum conditions which shows that molecular oxygen dissociates completely below 40 K on Cu(001) surface [24].

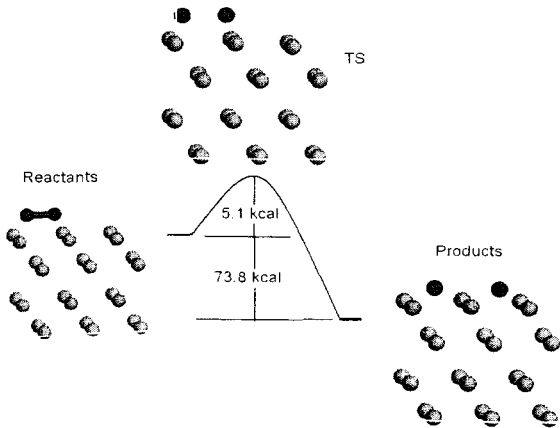


Figure 2: Dissociation mechanism for the reaction from an oxygen molecule adsorbed horizontally at a bridge-bridge site to two oxygen atoms adsorbed on hollow sites.

Table 5: Parameters of the transition state for the reaction from an oxygen molecule adsorbed horizontally at a bridge-bridge site to two oxygen atoms adsorbed on hollow sites.

Parameter	Value
O-O (Å)	1.95
Cu-O (Å)	1.88
⊥ Cu-O (Å)	1.27
Δd_{12} (%)	-0.27
Barrier Energy (kcal/mol)	5.1

The reaction pathway for the dissociative adsorption of O₂ starting from our most stable vertically oriented configuration is shown in Fig. 3. The corresponding transition state parameters for this reaction pathway are shown in Table 6. The activation energy for this reaction has been calculated to be 1.5 kcal/mol. The equivalent temperature for this energy is around 20 K. The distance between the oxygen atoms for the transition state was found to be 1.95 Å with the O-O bond being aligned at 62.5° to the horizontal.

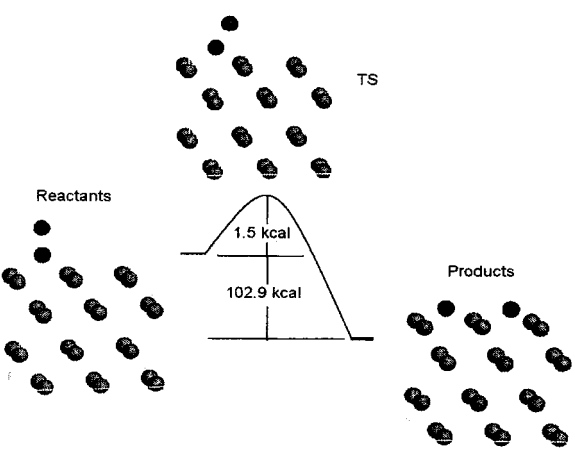


Figure 3: Dissociation mechanism for the reaction from an oxygen molecule adsorbed vertically at a hollow site to two oxygen atoms adsorbed on hollow sites.

Table 6: Parameters of the transition state for the reaction from an oxygen molecule adsorbed vertically at a hollow site to two oxygen atoms adsorbed on hollow sites.

Parameter	Value
O-O (Å)	1.95
Cu-O (Å)	1.88
⊥ Cu-O (Å)	0.994
∠O-O with the horizontal (°)	62.5
Δ <i>d</i> ₁₂ (%)	-1.1
Barrier Energy (kcal/mol)	1.5

4. Summary

In this paper we have investigated two dissociation reaction pathways for an oxygen molecule over the Cu(001) surface with application to formation of PCDD/F in combustion. The first pathway corresponds to the dissociation from a horizontally adsorbed O₂ to two adsorbed O atoms, while the second pathway constitutes the dissociation from a vertically adsorbed O₂ to two adsorbed O atoms. The calculated barrier energies are 5.1 and 1.5 kcal/mol for the first and second reaction pathways, respectively. Firstly, these results show that although O₂ is more stable when adsorbed horizontally on the Cu(001) surface, the vertically adsorbed O₂ configuration requires less

energy to dissociate. Secondly, these results show that the catalytic action of the Cu(001) surface can provide, with negligible energy input, the atomic oxygen required for the Deacon reaction. This is in contrast to oxygen dissociation in the gas phase which requires 146.6 kcal/mol of activation energy.

Acknowledgments

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