# A first-principles density functional study of chlorophenol adsorption on $Cu_2O(110):CuO$

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First-principles density functional theory and a periodic-slab model have been employed to explore the adsorption of a two-chlorophenol molecule on a $Cu_2O(110)$ surface containing surface Cu–O bonds, namely, the $Cu_2O(110):CuO$ surface. The two-chlorophenol molecule is found to interact very weakly with the $Cu_2O(110):CuO$ surface, forming several vertical and flat orientations. These weakly bound states tend to result from interaction between the phenolic hydrogen and an oxygen surface atom. The formation of a two-chlorophenoxy moiety and an isolated hydrogen on the $Cu_2O(110):CuO$ surface from a vacuum two-chlorophenol molecule is determined to have an endothermicity of 8.2 kcal/mol (0.37 eV). The energy required to form a two-chlorophenoxy radical in the gas phase is also found to be much smaller when assisted by the $Cu_2O(110):CuO$ surface than direct breaking of the hydroxyl bond of a free two-chlorophenol molecule. The calculated binding energy of a two-chlorophenoxy radical adsorbed directly onto the $Cu_2O(110):CuO$ surface is −12.5 kcal/mol (0.54 eV). The $Cu_2O(110):CuO$ and Cu(100) surfaces are found to have similar energy barriers for forming a surface-bound two-chlorophenoxy moiety from the adsorption of a two-chlorophenol molecule. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3123534]

## I. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are a class of organic pollutants formed invariably as unwanted products in all thermal systems where chlorine is present.[1,2] PCDD/Fs are formed through a series of complex reactions in the gas phase, as well as through catalyzed reactions. It is believed that 70% of the yield of PCDD/Fs arises from reactions assisted by metal species. One of the major experimentally predicted routes for their formation involves catalytically assisted coupling of precursors, especially chlorinated phenols, in the temperature region of 200–400 °C.[3] It is known that in the actual combustion environment, copper-based compounds are always present in the fuel feed and hence subsequently in the formed ash. It is also well documented in the literature that copper species, in particular copper oxides, are the most efficient surfaces in catalyzing the formation of PCDD/F compounds from chlorinated phenols.[3–5] However, the exact mechanism and the intermediate steps, especially the nature of the interactions of chlorophenols with copper oxide surfaces, are not well understood.

The formation of a 2-chlorophenoxy moiety following the breaking of the hydroxyl group in a 2-chlorophenol molecule on the CuO surface, constitutes a central step in a detailed kinetic model that describes the formation of PCDD/Fs from the adsorption of 2-chlorophenol on CuO.[4,5] This assumption is supported by the detection of an oxygen-centered 2-chlorophenoxy moiety on the CuO surface upon adsorption of 2-chlorophenol using an electron paramagnetic resonance technique.[6,7] The adsorbed 2-chlorophenoxy moiety is then transformed into a chlorophenolate (the anion form of 2-chlorophenoxy) via an electron transfer from the copper oxide surface.[6,7] The chemisorption of a 2-chlorophenol molecule on the CuO surface was shown to be accompanied by CuO reduction into Cu and mainly $Cu_2O$.[6]

Two mechanisms have been proposed for the formation of PCDD/Fs.[6,7] The Langmuir–Hinshelwood mechanism, which involves coupling of two adsorbed chlorophenolate moieties forming PCDFs, and the Eley–Rideal mechanism where the adsorbed chlorophenolate reacts with a gaseous chlorophenol molecule to produce PCDDs. Central to obtaining a better understanding of these mechanisms is the need to survey all possible interaction modes between chlorophenols and copper oxide surfaces. In a recent study,[8] we have addressed reactions between a 2,4,5-trichlorophenol molecule and an isolated CuO dimer, with an emphasis on the pathways which produce the 2,4,5-trichlorophenoxy radical through the abstraction of the hydroxyl H by the isolated CuO dimer. The process was found to be highly exothermic and facile. While our simplified model using an isolated CuO dimer accounts satisfactorily for the main experimental fea-

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tures for the interaction between chlorophenols and CuO surfaces, a better representation is needed to describe an extended copper oxide surface.

Interaction between an oxygen molecule and a clean copper surface has been studied experimentally[9–11] and theoretically.[12–16] These studies indicate that oxygen interaction with copper surfaces forms a thin layer of $Cu_2O$ that grows in a layer-by-layer fashion. This highlights the importance of studying clean $Cu_2O$ surfaces and the reactions that occur upon them.

Soon *et al.*[16] investigated the relative stability of the three low-index $Cu_2O$ surfaces, namely, (111), (110), and (100), in addition to different surface terminations of these three surfaces, using the so-called "*ab initio* atomistic thermodynamics" approach.[17,18] Their principal aim was to determine the most stable $Cu_2O$ surfaces for a wide range of temperature, pressure, and oxygen concentration to simulate the conditions appropriate to catalytic processes. For conditions under which PCDD/Fs are formed, two surfaces are found to be more stable than other surfaces: the $Cu_2O(110):CuO$ surface in which the outermost layer contains both O and Cu atoms (surface Cu–O bonds) and $Cu_2O(111)-Cu_{CuS}$ which has a vacant Cu position. In this study, we investigate the interaction between a 2-chlorophenol molecule and the $Cu_2O(110):CuO$ periodic surface. The results are compared with those derived from our recent work on the adsorption of a 2-chlorophenol molecule on clean copper surfaces[19,20] in order to explore systematically the effect of various copper species in assisting the formation of PCDD/Fs.

## II. COMPUTATIONAL METHODS

The Vienna *ab initio* simulation package (VASP) (Ref. 21) has been used for all of the geometry optimization and total energy calculations reported in this paper. Spin-polarized calculations have been performed using the generalized gradient approximation (GGA) of Perdew and Wang (PW91) (Ref. 22) for exchange and correlation. The ionic cores are represented by projector augmented wave (PAW) potentials.

The calculations were performed for a slab comprising a $(2\times2)$ surface unit cell and up to six atomic layers (see Sec. III A 2). A vacuum thickness of at least 10 Å was used to separate each slab from its neighboring images along the $z$ direction (normal to the surface). Generally, the two top-most layers of our slab and the molecule were allowed to fully relax, while the remaining layers were kept fixed. Integrations over the first Brillouin zone were performed using the four special **k**-points in the irreducible symmetry element of the surface Brillouin zone proposed for a rectangular cell by Cunningham.[23] Tests performed using a 16 special **k**-point set only changed the total energies by a few meV. For each geometry optimization, the total energy was converged to an accuracy of $1.0\times10^{-5}$ eV, and the forces on each ion to an accuracy of 0.01 eV $Å^{-1}$. Any dipole effects along the $z$-direction have been compensated by introducing a dipole vector with the same value in the opposite direction. Binding energies have been calculated using the geometries optimized with a 350 eV energy cutoff. Using a 500 eV energy cutoff for one of the structures was found to change the binding energy by only 6.0%. These binding energies were calculated as the difference between the total energy of the optimized chemisorbed structure, and the total energy of the noninteracting molecule and substrate in the same supercell.

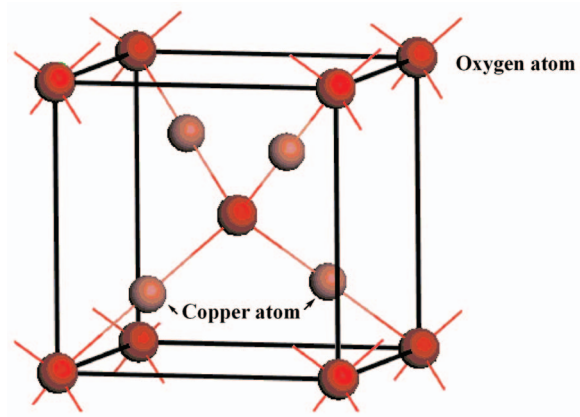


FIG. 1. (Color) Unit cell of bulk $Cu_2O$.

Reaction barriers for two key reactions have been determined by constructing energy paths consisting of eight intermediate images between the initial and final states using the nudged elastic band (NEB) method[24,25] as implemented in the VASP code. The eight intermediate images were allowed to relax varying the same atoms as for the optimization of the initial and the final states until a minimum energy path was formed for which all of the perpendicular forces to this path are negligibly small.

## III. RESULTS AND DISCUSSION

### A. Bulk $Cu_2O$, $Cu_2O(110):CuO$ surface and 2-chlorophenol molecule

#### *1. Bulk* $Cu_2O$

We first validated the adopted methodology by calculating the lattice constant of bulk $Cu_2O$. As can be seen from Fig. 1, each oxygen atom in bulk $Cu_2O$ is coordinated by four copper atoms (forming a tetrahedron), and each oxygen layer is sandwiched between two copper layers. The lattice constant was determined by plotting the variation in the energy with the volume of the unit cell of bulk $Cu_2O$ shown in Fig. 1. The lattice constant fitting was performed using a

TABLE I. Calculated geometrical parameters for bulk $Cu_2O$.

| Method | Lattice constant (Å) | Cu–O (Å) | Cu–Cu (Å) |
|---|---|---|---|
| This work (GGA-PAW) | 4.31 | 1.87 | 3.05 |
| GGA-PAW[a] | 4.31 | 1.87 | 3.05 |
| HF[b] | 4.28 | 1.85 | 3.03 |
| GGA-U.S.[a] | 4.32 | ⋯ | ⋯ |
| GGA-PBE[c] | 4.34 | 1.88 | 3.07 |
| Expt.[d] | 4.27 | 1.85 | 3.01 |

[a]Reference 27.
[b]Reference 28.
[c]Reference 29.
[d]References 30 and 31.

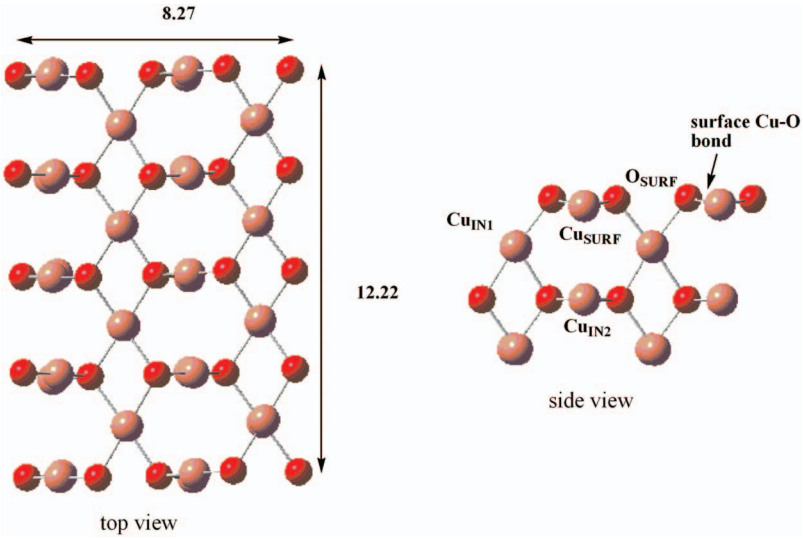


FIG. 2. (Color) Top and side views of the $2\times2$ unit supercell of the $Cu_2O(110):CuO$ surface. Dimensions are in angstrom.

$8\times8\times8$ Monkhorst–Pack grid.[26] The calculated lattice constant was 4.31 Å. In Table I, we compare our calculated geometry for bulk $Cu_2O$ with other experimental and theoretical values. Our results are seen to agree exactly with those obtained by Jiang *et al.*[27] using the same method and are also in good agreement with both experiment and other theoretical calculations.

### 2. $Cu_2O(110):CuO$ *surface*

A $(2\times2)$ supercell of the $Cu_2O(110):CuO$ surface was constructed from the $(1\times1)$ unit cell presented by Soon *et al.*[16] Our optimized substrate structure is displayed in Fig. 2, and our geometrical parameters compared with the results of Soon *et al.*[16] in Table II. We observe that the two sets of data agree quite well. We have also found that the geometrical parameters in Table II change by less than 0.005 Å when allowing three layers to relax instead of two or when using a six-layer slab and allowing the four top-most layers to relax.

### 3. 2-chlorophenol molecule

In a previous study,[20] using various theoretical methods, we obtained the ground state structure of the 2-chlorophenol molecule and its derivative radical, the 2-chlorophenoxy radical, which forms after the loss of the H atom from the hydroxyl group. The structures that we determined for the 2-chlorophenol molecule and 2-chlorophenoxy radical are shown in Fig. 3. In all structural optimizations, the *cis* form of the 2-chlorophenol molecule has been employed as it is slightly more stable than its *trans* counterpart. The corresponding structural parameters are presented in Table 1 in Ref. 20.

TABLE II. Bondlengths in the $Cu_2O(110):CuO$ surface. Atom labels are given in Fig. 2.

| | This work (Å) | Soon *et al.*[a] (Å) |
|---|---|---|
| $O_{surf}-Cu_{surf}$ | 1.82 | 1.84 |
| $O_{surf}-Cu_{IN1}$ | 1.83 | 1.84 |
| $Cu_{surf}-Cu_{IN2}$ | 2.84 | 2.78 |
| $Cu_{surf}-Cu_{surf}$ | 3.06 | 3.05 |

[a]Reference 16.

## B. Adsorption of 2-chlorophenol on the $Cu_2O(110):CuO$ surface

### 1. Molecular adsorption

Several flat and vertical configurations have been considered for the 2-chlorophenol molecule on the $Cu_2O(110):CuO$ surface. The optimized flat and vertical structures are shown in Figs. 4 and 5, respectively. Binding energies are given in Table III.

As can be seen from the bond distances shown in Figs. 4 and 5, and the calculated binding energies in Table III, chlorophenol is very weakly bound to the $Cu_2O(110):CuO$ surface. These results are very similar to those reported for the interaction of a chlorophenol molecule with clean copper surfaces.[19,20] Most of the structures in Figs. 4 and 5 are characterized by the formation of a weak bond between the hydrogen in the hydroxyl group of the 2-chlorophenol molecule and a surface oxygen ($O_{surf}$). Also, these structures exhibit to a large extent the geometry of a free chlorophenol molecule. Since all of these molecular structures are very weakly

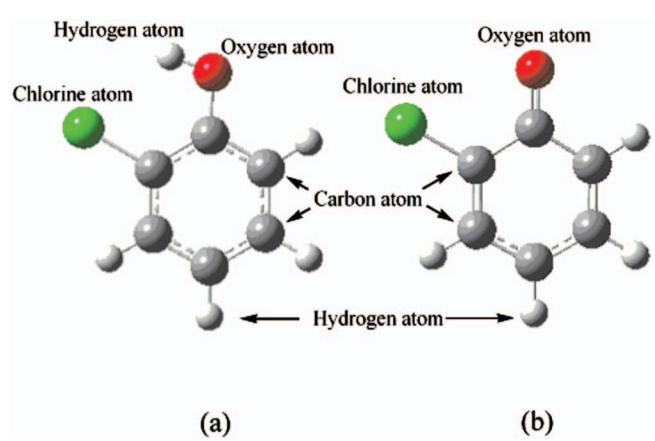


FIG. 3. (Color) Structures of (a) the *cis*-2-chlorophenol molecule and (b) the 2-chlorophenoxy radical. In the *trans* conformer, the hydroxyl H is pointing away from the chlorine atom.

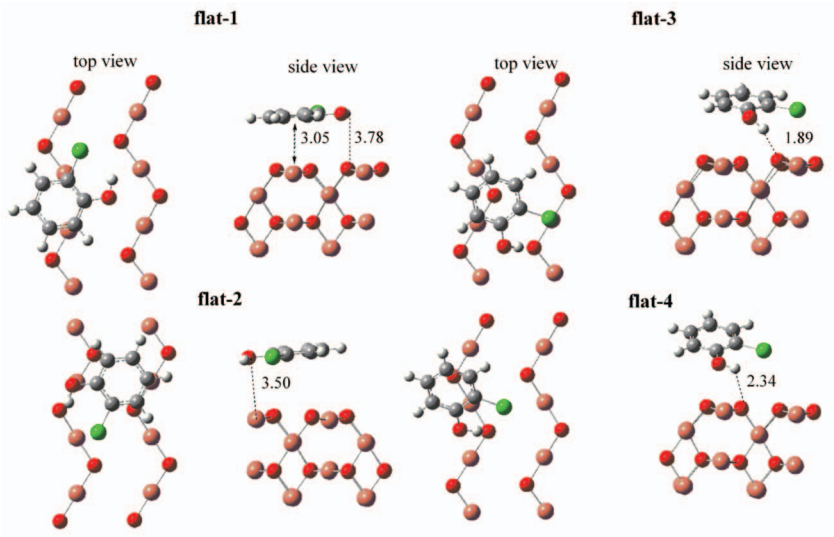


FIG. 4. (Color) Optimized structures for flat adsorption of a 2-chlorophenol molecule on the $Cu_2O(110):CuO$ surface. Reported distances are in angstrom. Only the first atomic layer is shown in the top views.

bonded to the surface, it is reasonable to assume that their adsorption from the vacuum onto the surface occurs without any energy barrier.

### 2. Dissociative structures

*a. Formation of 2-chlorophenoxy moiety* Dissociation of the hydrogen atom from the hydroxyl (OH) group of the 2-chlorophenol molecule results in the formation of a 2-chlorophenoxy moiety on the $Cu_2O(110):CuO$ surface. Two possible resultant structures are shown in Fig. 6. In structure D-1, both the 2-chlorophenoxy radical and the dissociated H are adsorbed on the same surface Cu–O bond, with the H atom attached to an $O_{surf}$ atom and the 2-chlorophenoxy moiety bonded to a $Cu_{surf}$ atom. The C–O bondlength in the adsorbed 2-chlorophenoxy moiety is 1.31 Å, intermediate between its length in the free 2-chlorophenol molecule (1.38 Å) and the free 2-chlorophenoxy radical (1.25 Å). The $O_{surf}$–$Cu_{surf}$ bondlength has increased by 0.14 Å from its equilibrium distance in the substrate (1.82 Å), and the $Cu_{surf}$ atom has moved upward by 0.3 Å. Formation of D-1 from the vacuum 2-chlorophenol is endothermic by 8.2 kcal/mol (0.36 eV). Transfer of the H atom in D-1 onto the $O_{surf}$ of a different Cu–O surface bond produces the structure (D-2) shown in Fig. 6(b). This structure is less stable than the structure D-1 by 4.0 kcal/mol (0.17 eV).

To estimate the reaction barrier for the formation of D-1 by means of the NEB method, we took the initial image to be the weakly bound vertical-1 structure shown in Fig. 5 and the final image to be the structure D-1. Since all of the vertical

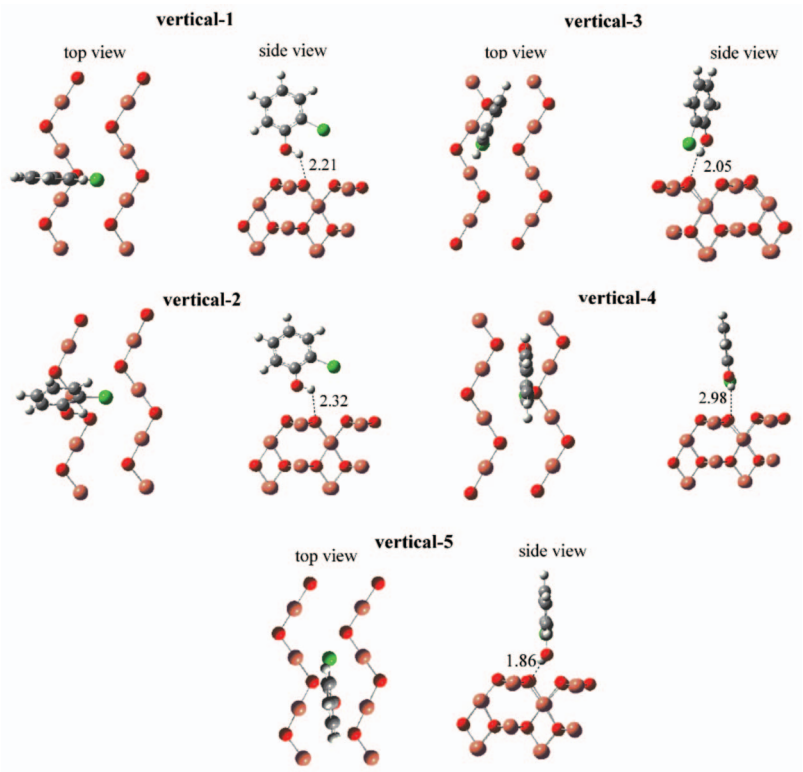


FIG. 5. (Color) Optimized structures for vertical adsorption of a 2-chlorophenol molecule on the $Cu_2O(110):CuO$ surface. Reported distances are in angstrom. Only the first atomic layer is shown in the top views.

TABLE III. Binding energies for the flat and vertical structures shown in Figs. 4 and 5. A negative value indicates that the adsorption process is exothermic. (1.0 eV=23.06 kcal/mol).

| Structure | Binding energy (kcal/mol) | Structure | Binding energy (kcal/mol) |
|---|---|---|---|
| Flat-1 | −2.0 | Vertical-2 | −2.0 |
| Flat-2 | −2.4 | Vertical-3 | −2.0 |
| Flat-3 | −3.4 | Vertical-4 | +0.5 |
| Flat-4 | −1.5 | Vertical-5 | −1.5 |
| Vertical-1 | −2.2 | | |

molecular structures bond to the surface in the same way and have similar stabilities, the vertical-1 structure can be taken as being representative of all the vertical structures for calculating the reaction barrier for the formation of the D-1 structure. To find the minimum energy path we created eight intermediate images by linearly interpolating between the initial and the final images and then optimized these images within the NEB method. The energy was found to change smoothly from that of the weakly bound initial state to the final product (adsorbed 2-chlorophenoxy+H) without passing through a reaction barrier. We can thus conclude that the amount of energy required to form the D-1 structure from an isolated 2-chlorophenol molecule above the $Cu_2O(110):CuO$ surface is 8.2 kcal/mol (0.36 eV). This value is 11.1 kcal/mol

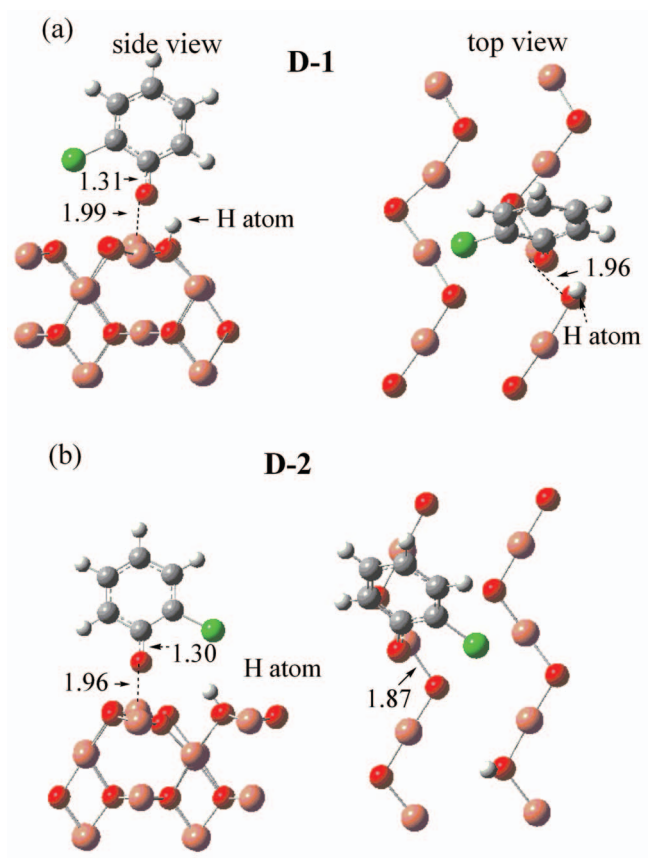


FIG. 6. (Color) Chemisorption of a 2-chlorophenoxy radical on the $Cu_2O(110):CuO$ surface in the optimized structures (a) D-1 and (b) D-2. Distances are in angstrom. Only the first atomic layer is shown in the top views.

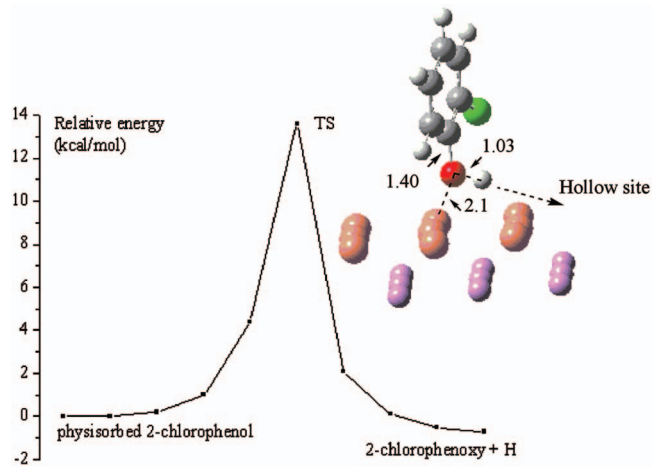


FIG. 7. (Color) Reaction pathway for the formation of a separately bonded 2-chlorophenoxy moiety and a hydrogen atom on the clean Cu(100) surface. The structure of the transition state is also shown. Distances are in angstrom.

(0.48 eV) lower than the value used by Khachatryan *et al.*[4] in their recent kinetic model for the formation of PCDD/Fs over a CuO surface.

Desorption of the 2-chlorophenoxy moiety into the vacuum from structures D-1 and D-2 was found to be endothermic by 8.5 kcal/mol (0.37 eV) and 12.5 kcal/mol (0.54 eV), respectively. These results (together with the above barrierless formation energy of 8.2 kcal/mol for D-1) indicate that the energy requirement for the formation of a gaseous 2-chlorophenoxy radical when assisted by the $Cu_2O(110):CuO$ surface is much less than the 83.0 kcal/mol (3.6 eV) required to break the hydroxyl bond in the gas phase.[8]

It is interesting to note that the formation of a 2-chlorophenoxy moiety is more thermodynamically preferred on the clean Cu(100) surface (−2.8 kcal/mol) (Ref. 20) than on the $Cu_2O(110):CuO$ surface (+8.2 kcal/mol). However, kinetic parameters are also important in determining which surface is more efficient in forming the 2-chlorophenoxy moiety. Thus, we have also calculated the reaction barrier for the Cu(100) surface. The calculated reaction pathway is plotted in Fig. 7. This figure describes the movement of the phenolic H from the O atom of the 2-chlorophenol molecule to its preferred hollow site on the Cu(100) surface. The initial state is a weakly bound state in which the 2-chlorophenol molecule is oriented vertically with the hydroxyl group pointing downward. The calculated reaction barrier is determined to lie 13.6 kcal/mol (0.59 eV) above the weakly bound 2-chlorophenol state on the Cu(100) surface or 11.5 kcal/mol (0.50 eV) above the 2-chlorophenol molecule in the vacuum. A comparison of the energetics of the Cu(100) and $Cu_2O(110):CuO$ surfaces associated with forming the 2-chlorophenoxy moiety is shown in Fig. 8. As stated above, the energy required for the $Cu_2O(110):CuO$ surface is 8.2 kcal/mol (0.36 eV), compared with 11.5 kcal/mol (0.50 eV) for the Cu(100) surface. We can thus conclude that these two surfaces require fairly similar energies in facilitating the formation of a 2-chlorophenoxy moiety.

In the conditions encountered in a real combustion environment, the 2-chlorophenoxy radical can be formed in the

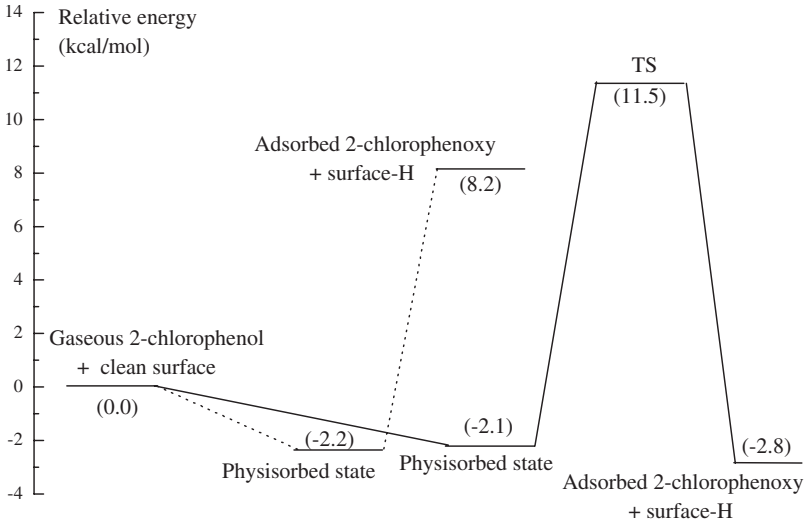


FIG. 8. Relative energies for the formation of a 2-chlorophenoxy moiety. The dotted and solid lines denote reaction paths for the $Cu_2O(110):CuO$ and Cu(100) surfaces, respectively.

gas phase via highly exothermic reactions with the O/H radical pool. In addition, the 2-chlorophenoxy radical is a stable persistent radical that can build up to an appreciable amount in the combustion reaction environment due to its very slow reaction with molecular oxygen.[32] As a result, we have also investigated the adsorption of an isolated 2-chlorophenoxy radical directly onto the $Cu_2O(110):CuO$ surface. By means of the NEB method, the reaction pathway for this adsorption process has been followed from a 2-chlorophenoxy radical in the vacuum to an adsorbed 2-chlorophenoxy moiety. We found that the adsorption process does not encounter a barrier and the adsorbed 2-chlorophenoxy has an energy of −12.5 kcal/mol (−0.54 eV) with respect to the vacuum 2-chlorophenoxy radical. The optimized geometry of the adsorbed 2-chlorophenoxy moiety on the $Cu_2O(110):CuO$ surface is very similar to that reported for the 2-chlorophenoxy moiety in the structure D-2 [see Fig. 6(b)]. It is interesting to note that the 2-chlorophenoxy moiety is more strongly bound to the clean copper surfaces, having binding energies of −40.6 kcal/mol (−1.76 eV) and −32.6 kcal/mol (−1.41 eV) for the Cu(100) (Ref. 19) and Cu(111) (Ref. 20) surfaces, respectively.

Due to the relatively small energy of 12.5 kcal/mol (0.54 eV) required to desorb a 2-chlorophenoxy moiety from the $Cu_2O(110):CuO$ surface, an equilibrium state comprising both chemisorbed and gaseous 2-chlorophenoxy radicals is most likely to dominate the adsorption process.

*b. Formation of phenyl moiety* Formation of a phenyl moiety through dissociation and the separate adsorption of a chlorine atom and a hydroxyl group on the Cu(100) (Ref. 20) and Cu(111) (Ref. 19) surfaces was shown to provide the most stable structures resulting from the interaction of a 2-chlorophenol molecule. We thus now turn to investigate the formation of a phenyl moiety on the $Cu_2O(110):CuO$ surface. In this section, we only consider energetics and geometries for the structures and not reaction barriers, as the considered structures are not precursors for the formation of PCDD/Fs.

Lomnicki and Dellinger[33] have investigated the formation of PCDD/Fs from the pyrolysis of 2-chlorophenol over a supported copper oxide catalyst in the temperature range of 200–500 °C. Despite the absence of oxygen, Lomnicki and Dellinger[33] found that 95% of the 2-chlorophenol molecules were consumed into CO and $CO_2$, and only about 0.5% were converted to PCDD/Fs. Due to the highly reducing conditions, the oxygen was assumed to have originated from the copper oxide surface. To model direct interaction between phenolic carbon atom and a surface oxygen atom, we have placed the dissociated hydroxyl group of a chlorophenol molecule above a $Cu_{surf}$ atom, and the unpaired C atom of the remaining 2-chlorophenol moiety above an $O_{surf}$ atom. The resulting optimized structure is shown in Fig. 9. The C–O bond is 1.41 Å which is close to the C–O distance in both the free 2-chlorophenol molecule and 2-chlorophenoxy radicals chemisorbed on the clean copper surfaces (1.37 Å). The formation of this chemisorbed structure is found to be unlikely, however, as it requires 39.1 kcal/mol (1.70 eV) of energy. Moving the OH group onto another copper surface atom also makes little difference to this energy value.

Finally, we explore dechlorination of a 2-chlorophenol molecule through chlorine abstraction by the surface, and the formation of a surface-bound OH-phenyl moiety. The resulting optimized geometry is shown in Fig. 10. The adsorbed chlorine forms an ionic Cu–Cl bond with length of 2.19 Å, and the OH-phenyl moiety is attached to an $O_{surf}$ atom via its

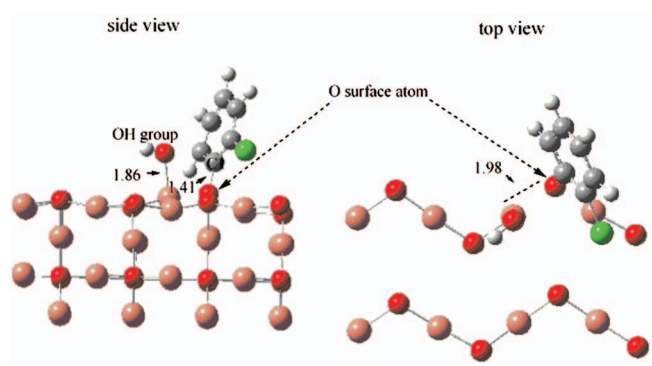


FIG. 9. (Color) Formation of a chemisorbed 2-chlorophenoxy moiety via the attachment of the dissociated OH group of a 2-chlorophenol molecule to a $Cu_{surf}$ atom and the bonding of the remaining fragment to an oxygen surface atom. Distances are in angstrom. Only the first atomic layer is shown in the top views.

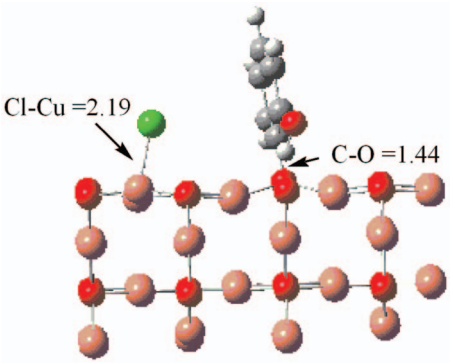


FIG. 10. (Color) Dechlorination of a two-chlorophenol molecule and the formation of a surface-bound OH-phenyl moiety (side view). Distances are in angstrom.

radical C site. The formation of this structure from a completely isolated 2-chlorophenol molecule requires 4.7 kcal/mol (0.20 eV). By contrast, the formation of similar dissociative structures on the clean copper surfaces was found to take place with considerable exothermicity.[19,20]

## IV. SUMMARY AND CONCLUSIONS

We have investigated the interaction between a 2-chlorophenol molecule and the $Cu_2O(110):CuO$ surface, which according to Soon *et al.*[16] is one of the two most stable $Cu_2O$ surfaces under pressure and temperature conditions corresponding to the formation of PCDD/Fs in combustion systems. The 2-chlorophenol molecule is found to adopt several different flat and vertical orientations in which it is bound to the $Cu_2O(110):CuO$ surface via a weak interaction between the phenolic H and a substrate surface oxygen atom.

The formation of a 2-chlorophenoxy moiety, which results from the fission of the phenolic O–H bond on the $Cu_2O(110):CuO$ surface, is found to be endothermic by 8.2 kcal/mol (0.37 eV), whereas it was exothermic by 2.8 kcal/mol (0.12 eV) on the Cu(100) surface. Reaction pathway calculations have shown that the energy required for O–H bond fission and the formation of a surface 2-chlorophenoxy moiety on the $Cu_2O(110):CuO$ surface is the same as the reaction energy (i.e., it is a barrierless reaction), while there is a net barrier of 11.5 kcal/mol (0.50 eV) on the Cu(100) surface. Reaction on these two surfaces, however, is more energetically favorable than the uncatalyzed process in the gas phase.

The adsorption of a 2-chlorophenoxy radical from the vacuum onto the $Cu_2O(110):CuO$ surface was found to occur without a barrier and to yield a binding energy of −12.5 kcal/mol, significantly less than the corresponding values reported for the clean copper surfaces (−40.6 kcal/mol (−1.76 eV) and −32.6 kcal/mol(−1.41 eV) for Cu(100) and Cu(111), respectively). Since the desorption barrier for a 2-chlorophenoxy moiety on the $Cu_2O(110):CuO$ surface is relatively small, it is likely that an equilibrium state forms between surface-bound 2-chlorophenoxy moieties and 2-chlorophenoxy radicals in the gas phase.

## ACKNOWLEDGMENTS

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