

Surface oxides of the oxygen–copper system: Precursors to the bulk oxide phase?

Aloysius Soon^{a,*}, Mira Todorova^a, Bernard Delley^b, Catherine Stampfl^a

^a School of Physics, The University of Sydney, Sydney 2006, Australia

^b Paul-Scherrer-Institut, CH-5232, Villigen PSI, Switzerland

Available online 30 June 2007

Abstract

To gain an initial understanding of the copper-based catalysts in commercially important chemical reactions such as the oxygen-assisted water–gas shift reaction, we performed density-functional theory calculations, investigating the interaction of oxygen and copper, focusing on the relative stability of surface oxides and oxide surfaces of the O/Cu system. By employing the technique of “*ab initio* atomistic thermodynamics”, we show that surface oxides are only metastable at relevant pressures and temperatures of technical catalysis, with no stable chemisorption phase observed even at very low coverage. Although exhibiting only metastability, these surface oxides resemble the bulk oxide material both geometrically and electronically, and may serve as a precursor phase before onset of the bulk oxide phase. Having identified the bulk oxide as the most stable phase under realistic catalytic conditions, we show that a Cu₂O(111) surface with Cu vacancies has a lower free energy than the stoichiometric surface for the considered range of oxygen chemical potential and could be catalytically relevant.

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Keywords: Density functional calculations; Corrosion; Oxidation; Surface oxides; Surface thermodynamics (including phase transitions); Atomistic thermodynamics; Copper

1. Introduction

The basic interaction between oxygen and metal surfaces is crucial to the fundamental understanding of the role of oxygen in a number of important technological processes, such as oxidation, corrosion and heterogeneous catalysis [1,2]. Many recent studies have shown that oxygen/transition metal (O/TM) systems exhibit a rich and complex surface phase space depending upon, e.g., pressure, temperature, and stoichiometry [1–16]. Clearly, having a precise knowledge of the detailed atomic structure is central in improving the performance of existing catalysts as well as developing new ones.

Increased awareness of clean energy technology in recent years has brought about a renewed interest in the water–gas shift (WGS) reaction in relation to fuel-cell tech-

nologies, where hydrogen is produced via partial oxidation and steam reforming of hydrocarbons and methanol [17]. Copper-based catalysts are known to be catalytically active for methanol synthesis, partial oxidation of methanol and the WGS reaction. The active site, the role of support oxides, and each detailed reaction mechanism are still however not well known or understood.

As a first step towards gaining insight into the microscopic mechanisms involved in these technologically important reactions, it is helpful to investigate the interaction of O with Cu and the formation of oxide structures [3]. In the present work, we focus on the (111) surface of Cu and report results of first-principles calculations for the relative stability of surface oxides, and oxide surfaces, with the former being thin oxidic structures formed on the copper metal surface and the latter cleaved crystallographic surfaces of the bulk oxide material. The O/Cu(111) system has been investigated both theoretically [3,18] and experimentally [19–29]. Recent ultra-high vacuum scanning

* Corresponding author.

E-mail address: aloyusius@physics.usyd.edu.au (A. Soon).

tunneling microscopy experiments [19] have shown that oxidation of the Cu(111) surface is extremely complex. Observed surface geometries are described as a ($\sqrt{73}R5.8^\circ \times \sqrt{21}R10.9^\circ$) structure (also known as the “44”-structure) and a ($\sqrt{13}R46.1^\circ \times 7R21.8^\circ$) structure (also known as the “29”-structure). These phases are thought to resemble the primary structure of one layer of $\text{Cu}_2\text{O}(111)$, consisting of a tri-layer repeat unit with each copper layer packed in between two layers of oxygen atoms. The surface unit cell of $\text{Cu}_2\text{O}(111)$ is approximately four times the surface unit area of Cu(111) and bears a hexagonal symmetry. These factors suggest that the bulk oxide formation could be achieved via a surface oxide phase.

Recently, we investigated surface oxide formation on Cu(111) using state-of-the-art density-functional theory (DFT) calculations where we used (4×4) surface unit cells to model the above-mentioned experimentally observed structures [3]. Using the approach of “*ab initio* atomistic thermodynamics” [7,8], we identify three low-energy oxidic structures, which are energetically preferred compared to chemisorption on the surface, even at very low coverages, yet are metastable compared to the bulk cuprous oxide at relevant pressures and temperatures of technical catalysis. These surface oxides are similar to those identified from density-functional theory (DFT) calculations of the (4×4) O/Ag(111) system [9]. However, for the latter system, such structures are stable with respect to the bulk silver oxide. Recently, a new (4×4) reconstruction of the Ag(111) surface has been proposed, which shows considerably better agreement with experimental results than all previously considered models [4,5]. Being in the same base metal group in the periodic table, we investigate in the present paper the relative stability of this structure for the O/Cu(111) system.

As mentioned above, the bulk cuprous oxide phase is thermodynamically stable at relevant catalytic conditions. From the experimental literature, it is often reported that a “ $\text{Cu}_2\text{O}(111)$ ”-like oxidic structure forms on an oxidized Cu(111) surface [19,27,29], hence as a first step, we investigate the relative stability of various terminations of bulk $\text{Cu}_2\text{O}(111)$ under relevant pressure and temperature conditions. Our results show a preference for non-stoichiometric (Cu-lean) defected surface.

2. Methodology

All the DFT calculations are performed using the generalized gradient approximation of Perdew, Burke and Ernzerhof [30] for the exchange–correlation potential as implemented in the DMol³ code. The DMol³ method is an all-electron code, which employs fast converging three-dimensional numerical integration to calculate the matrix elements occurring in the Ritz variational method. More details of the DMol³ code can be found elsewhere [31].

All surface structures are modeled in a supercell geometry, employing a symmetric slab consisting of five (111) Cu

layers, with the oxidic structures constructed on both sides. A vacuum region of 25 Å ensures the decoupling of repeated slabs. The surface oxide layer and two outermost Cu layers are fully relaxed. The wave-functions are expanded in terms of a double-numerical quality localized basis set with a real space cutoff of 9 Bohr. Brillouin-zone integrations are performed using a ($12 \times 12 \times 1$) Monkhorst–Pack grid with 19 **k** points in the irreducible Brillouin-zone (IBZ) of a (1×1) cell and a thermal broadening of 0.1 eV. To obtain the same sampling of the reciprocal space for larger surface cells, this number is reduced accordingly. To model the $\text{Cu}_2\text{O}(111)$ surfaces, we employ a (1×1) surface unit cell and use a ($8 \times 8 \times 1$) Monkhorst–Pack grid with 10 **k** points in the IBZ. We use a 15-atomic layer slab, separated by a vacuum region of 33.5 Å, and fully relax the 12 outermost layers. The high accuracy of the basis set is described in Ref. [3].

To take into consideration realistic experimental conditions, the effect of temperature and pressure is included by taking into account the surrounding gas phase in terms of “*ab initio* atomistic thermodynamics” [7,8]. This approach allows the determination of the lowest-energy surface structure, for given conditions of a surrounding gas phase. More details of the methodology can be found elsewhere [2,3].

3. Results and discussion

3.1. Surface oxides

In our earlier publication [3], we carried out detailed DFT calculations to investigate on-surface and sub-surface adsorption of O on Cu(111), as well as the stability of surface oxide structures. To replicate the so-called “44”- and “29”-structures, we used a (4×4) supercell to model various possible configurations of different oxygen content. As the surface area of a (1×1) unit cell of $\text{Cu}_2\text{O}(111)$ is approximately four times that of Cu(111), the (4×4) supercell is deemed a good starting point to mimic these superoxide structures seen experimentally. Our findings may be summarized as follows: For conditions typical of technical catalysis (e.g., $p = 1$ atm, $T = 600$ K), the bulk oxide is thermodynamically most stable; however, if formation of the fully oxidized surface is prevented due to kinetic hindering, thin surface oxides are found to be energetically preferred compared to chemisorption on the surface, even at very low coverage. The main results are displayed in Fig. 1A, which shows the Gibbs free energy of the lowest-energy structures versus the oxygen chemical potential [8]. By including the effects of pressure and temperature through the dependence of the oxygen molecule, we correlate the oxygen chemical potential with a pressure scale for selected temperatures. For reference, we have included the result for chemisorption of O on Cu(111) at coverage 0.25 ML, as calculated using a (2×2) surface unit cell. It can be seen that for values of the oxygen chemical potential ($\Delta\mu_{\text{O}}$) of less than -1.65 eV, the clean Cu(111) surface is

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