First-principles studies of oxygen chemisorption on Co(0001)

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S.H. Ma *, Z.Y. Jiao, T.X. Wang, X.Q. Dai

College of Physics and Information Engineering, Henan Normal University, Xinxiang, Henan 453007, China

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ABSTRACT

We perform density-functional theory calculations to study the adsorption of oxygen on Co(0001) for a wide coverage range from 0.11 to 2.0 monolayers (ML), including on-surface and subsurface adsorption. Present results demonstrate that atomic oxygen prefers on-surface hollow sites and a local p(2 × 2)-O overlayer is formed at 0.25 ML, in agreement with experimental observation. Upon one full monolayer oxygen on Co(0001), the incorporation of oxygen under the first Co layer is found to be exothermic and the adsorption energy changes very small with the increase of subsurface oxygen, implying an attractive interaction between adatoms O. Other coverage-dependent properties especially the *d*-band electronic structure modifications and the two-dimensional phase diagram are discussed in comparison with similar systems. Present results indicate that with the completion of the full monolayer oxygen on Co(0001), subsequent O atoms incorporate into the subsurface with an easy site-switch and finally it preferentially leads to an O–Co–O trilayer on top of the Co(0001) surface.

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1. Introduction

The chemisorption of oxygen on transition metal (TM) surface is of high importance for heterogeneous oxidation (partial oxidation) catalysis and this has motivated large numbers of studies on oxygen–metal interactions at low index surfaces in order to gain a better understanding of the underlying mechanisms [1,2]. Theoretically, oxygen adsorbed on such TMs as 3d: Fe [3], Ni [4], Cu [5], 4d: Ru [6,7], Rh [8,9], Pd [10,11], Ag [12], 5d: Re [13], Ir [14–16], Pt [17,18], Au [10,17] and metal Pb [19] surfaces has been studied in more detail. These studies highlight the complex nature of surface atomic structures that can form for oxygen/TM systems, and how they depend sensitively upon the "environment", e.g. the pressure and temperature.

Cobalt-based catalyst, as an efficient catalyst in Fisher–Tropsch synthesis (FTS), a possible oxidation of its surface has often been perceived as leading to an inactive surface oxide layer, poisoning the catalytic reaction [20,21]. Thus, there are considerable experiments devoted to the interaction of oxygen with Co(10 1¯ 0) [22,23], Co(11 2¯ 0) [24–26] and Co(0001) [27–32] surfaces by means of low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), change of work function and UV photoelectron spectroscopy (UPS) techniques. Previously, Bridge et al. [28] proposed that the chemisorption of O on Co(0001) readily undergoes conversion to cobalt oxide even at room temperature, and at higher temperatures CoO growth proceeds. Castro et al. [29] reported that oxygen dissociatively adsorbed on Co(0001) forming a p(2×2)-O phase at T≥120K, after reaching a specific coverage (0.5 ML), oxygen diffuses into the bulk forming cobalt oxides. Based on the spin resolving photoelectron spectroscopy analysis, Getzlaff

et al. [30,32] found that oxygen adsorption on Co(0001) films leads to three different oxygen species (chemisorbed oxygen overlayer, CoO and Co_3O_4) depending on oxygen exposures and temperatures. Recently, Huang et al. [33] reported that the presence and nature of oxygen species on Co(0001) exert great influence on its reactivity toward H_2O. Theoretically, only limited information on the O/Co(0001) system [34–36] has been provided by far, such as the effect of oxygen adsorption on the surface magnetism. However, a systematic study of coverage-dependent behaviors for oxygen adsorbed on Co(0001) including the on-surface and subsurface, is still lacking.

In this paper, we have performed a first-principles calculation for oxygen on-surface and subsurface adsorption on Co(0001) surface in a wide coverage range from 0.11 to 2.0 ML. Coverage-dependent adsorption properties of energetics, site-preference, atomic and electronic structures are systematically discussed in comparison with similar systems. Especially, the surface *d*-band structure modifications induced by oxygen on-surface adsorption are analyzed, and the thermodynamic phase diagram is also discussed by applying *ab initio* atomistic thermodynamics [2].

2. Computational methods

All spin-polarized calculations are performed using the DFT total energy Vienna *ab initio* simulation package (VASP) code [37]. We employ the projector augmented-wave method (PAW) [38] and the revised Perdew–Wang (RPBE) generalized gradient approximation (GGA) for the exchange-correlation functional [39]. A cutoff energy of 380 eV is used.

The substrate Co(0001) surface is modeled by a five-layer cobalt atom slab with a vacuum layer of 12 Å. We consider oxygen coverages from 0.11 ML to 2.0 ML using these p(3×3), p(2×2) and p(1×1) surface unit cells (SUC), in which oxygen adsorption in various on-surface and

subsurface sites is studied as explained below. The topmost three Co layers and the oxygen atoms adsorbed on one side of the slab are allowed to fully relax until the final forces acting on the atoms are less than 0.025 eV/Å. For the Brillouin-zone (BZ) integration, a Γ-centered 12 × 12 × 1 Monkhorst–Pack grid [40] for the (1 × 1) SUC and (6 × 6 × 1) for other SUCs are chosen, yielding 43 and 21 irreducible k-points, respectively. The total energy variation is found to be less than 40 meV when changing the energy cutoff from 350 to 400 eV.

The adsorption energy (E_{ad}^O) per oxygen atom on the surface is defined as

$$E_{ad}^O = -\frac{1}{N_O}\left(E_{O/Co(0001)} - E_{Co(0001)} - N_O \cdot E_O\right) \qquad (1)$$

where N_O, $E_{O/Co(0001)}$, $E_{Co(0001)}$ and E_O are the number of oxygen atoms in the SUC, the total energies of adsorbate–substrate system, clean surface, and free oxygen atom, respectively. The adsorption energy ($E_{ad}^{\frac{1}{2}O_2}$) can also be referenced to the energy which the O atom has in the gas-phase oxygen molecule by subtracting half the binding energy $E_b^{O_2}$, displayed as the formula (2),

$$E_{ad}^{\frac{1}{2}O_2} = E_{ad}^O - \frac{1}{2}E_b^{O_2} \qquad (2)$$

In these cases, positive energy values of $E_{ad}^{\frac{1}{2}O_2}$ and E_{ad}^O indicate that the adsorption is exothermic (stable).

Surface dipole moment μ (in Debye) is evaluated using the Helmholtz equation,

$$\mu = \frac{A\Delta\Phi}{12\pi\theta_O} \qquad (3)$$

where A, $\Delta\Phi$ and θ_O are the surface area in Å^2 per (1 × 1) SUC, work function (WF) change in eV and oxygen coverage, respectively.

In order to investigate the effect of pressure and temperature on the stability of various structures, the Gibbs free energy of formation $\gamma(T,p,\theta_o)$ [15] per Å^2 for oxygen adsorption on Co(0001), is approximated in terms of the adsorption energy, $E_{ad}^{\frac{1}{2}O_2}$,

$$\gamma(T, p, \theta_o) = -\frac{\theta_O}{A}\left[E_{ad}^{\frac{1}{2}O_2} + \frac{1}{2}\Delta\mu(T, p)\right] \qquad (4)$$

The temperature (T) and pressure (p) dependence is mainly given by the chemical potential of oxygen molecules $\Delta\mu(T,p)$, which is defined as $\Delta\mu(T,p) = \left[\tilde{\mu}_{O_2}(T,p^0) + k_BT\ln\left(\frac{p}{p^0}\right)\right]$ according to Ref.[40]. $\tilde{\mu}_{O_2}(T,p^0)$ is the T-dependent oxygen chemical potential at the standard pressure $p^0 = 1$ atm, which is given in Ref. [41].

3. Results and discussion

3.1. Reference values

Within GGA-RPBE, previous calculations of hexagonal-close-packed (hcp) bulk Co lattice constants are a = 2.52 Å and c/a = 1.62 [42], which differ from the experimental values of a = 2.507 Å and c/a = 1.62 [43] by 0.5%. Calculated bulk modulus and cohesive energy per Co atom are 210 GPa and 4.98 eV, in good agreement with the experimental values of 190 GPa [44] and 4.39 eV [45], as well as other reported DFT results of 215 GPa and 5.14 eV [46]. For the clean Co(0001) surface, our previous calculations [47] show that the top interlayer spacing is contracted by 1.8% and the second Co interlayer spacing exhibits an expansion of 1.6% with respect to the bulk cobalt. The magnetic moment of surface Co layer is enhanced to 1.72μ_B compared to the bulk cobalt of 1.65μ_B.

Placing a molecule O$_2$ in a large supercell of 15 × 16 × 17 Å^3 with spin-polarized calculations, we obtained its O–O bond length, stretch vibrational frequency and binding energy per atom of a free oxygen molecule

$\frac{1}{2}E_b^{O_2}$, which are corresponding to 1.23 Å, 1580 cm^{-1} and 2.89 eV/O. These are consistent with experimental data of 1.21 Å, 1580 cm^{-1} and 2.56 eV/O [14], and the typical overestimation of the O$_2$ binding energy is well-known in literature [5,14,17].

3.2. Coverage-dependent properties of O/Co(0001)

3.2.1. Energetics and site preference for $\theta_O \leq 1.0$ ML

On Co(0001) surface, we considered atom O adsorption in the three-fold hcp- and fcc-hollow sites for various overlayers: p(3 × 3)-O, p(2 × 2)-nO (n = 1, 2, 3, 4) corresponding to oxygen coverage θ_O = 0.11, 0.25, 0.5, 0.75 and 1.0 ML, respectively. Calculated adsorption energies (E_{ad}^O) are presented in Fig. 1 and one can see from Fig. 1(a) that the hcp-hollow site is preferred energetically, leading the fcc-hollow site by 0.1 eV at a low coverage of 0.11 ML. Yet, upon the coverage increasing, the adsorption energy difference between oxygen in hcp- and fcc-hollow site becomes small and at 1.0 ML the site preference of O atom in hcp- or fcc-hollow site is negligible, similar to O/Ru(0001) [6]. At 0.25 and 0.5 ML, our calculations of 5.56 and 5.02 eV compare well with the values of 5.39 and 4.97 eV obtained by Huo et al. [36] using the ultrasoft pseudopotentials, respectively. As shown in Fig. 1(a), a clear dip in adsorption energy at 0.25 ML shows that a local (2 × 2)-O phase is the most favorable, in accordance with the experimental observation of a (2 × 2)-O island formation on Co(0001) [27]. With the increase of coverage above 0.25 ML, the adsorption energy strongly
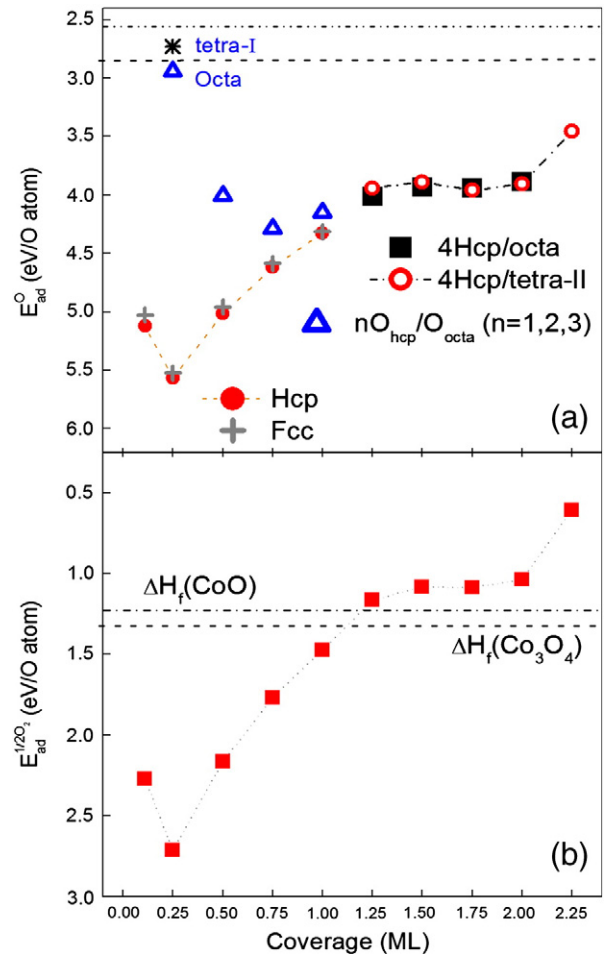
Fig. 1. Calculated adsorption energy E_{ad}^O (a) as a function of oxygen coverage for most favorable configurations of O adsorbed on-surface and subsurface sites on Co(0001), along with those of $E_{ad}^{\frac{1}{2}O_2}$ (b) with respect to molecular oxygen. (The horizontal upper and lower lines in (a) are half the experimental and theoretical binding energies of O$_2$, and those in (b) denote the experimental values of the enthalpy of formation for bulk cobalt oxides rock-salt CoO and normal spinel Co$_3$O$_4$, respectively.)