

Density Functional Theory study of electric field effects on CO and OH adsorption and co-adsorption on gold surfaces

Andrey A. Koverga^a, Stefan Frank^a, Marc T.M. Koper^{a,b,*}

^a Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

^b Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

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ABSTRACT

A Density Functional Theory (DFT) study of CO and OH adsorption on Au(111) and Au(110) surfaces is presented. The analysis includes the effect of an external negative electric field on adsorption characteristics such as binding energies, binding geometries, charge distribution and vibrational frequencies, both on CO and OH individually and in co-adsorbed geometries. The minimal energy pathways for COOH formation from CO and OH co-adsorbed on Au(111) and Au(110) were also calculated. The ability of CO to enhance the adsorption of OH on gold is discussed in relation to the surface structure of gold and changes in the work function as induced by the adsorption of CO.

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1. Introduction

Gold catalysis has become the subject of numerous experimental [1–8], and computational studies [9,10] in recent years. Several reviews on the subject have also appeared [11–13]. As a noble metal, gold is considered catalytically inactive, but it appears to show a remarkable activity for the oxidation of carbon monoxide both in the gas phase and in aqueous (alkaline) solution. The exact mechanism for this activity is still not clear and is the subject of numerous debates. The unexpected activity of gold, as first studied in great detail in gas-phase catalysis by Haruta et al. [1–3], could have promising applications for fuel cells in for instance the selective removal of CO from the gaseous hydrogen fuel.

As the catalytic activity of gold seems to be limited to small gold nanoparticles on an oxidic support or on TiC, models for the catalytic activity of gold are mainly limited to such systems. However, under aqueous electrochemical conditions, single crystalline gold is also very active for the oxidation of carbon monoxide, primarily in alkaline solution [14]. Our group has recently ascribed the high activity of gold for CO oxidation in alkaline media to the ability of CO to promote the adsorption of its oxidant, namely OH [15–17]. This effect was also assumed to be related to the appearance of an unusual voltammetric peak at 0.4 V vs RHE on

Au(111) in the presence of a small amount of irreversibly adsorbed CO on the surface, but in the absence of CO in solution [18]. Further studies combining experimental Fourier Transform Infrared Spectroscopy combined with Density Functional Theory (DFT) calculations have suggested a role for OH⁻ in stabilizing the adsorption of CO on gold low index single-crystalline surfaces in alkaline media. Moreover, it was found that the amount of CO irreversibly adsorbed on Au(111) depended on the adsorption potential, more negative adsorption potentials leading to a higher amount of CO on the surface [19]. On Au(111), all three adsorption geometries (atop, bridge, hollow) were observed. On Au(110), only atop adsorption was observed in the FTIR experiments in alkaline media. More negative adsorption potentials yielded a higher coverage of CO on the Au(110) surface, similar to Au(111). Interestingly, it was found CO irreversibly adsorbed on Au(111) in alkaline media may promote the oxidation of certain alcohols, but no such effect was observed for Au(110) [17]. In acidic media, there is no evidence for the irreversible bonding of CO to single-crystalline Au, and CO adsorption states are observed only in the presence of CO in solution [19–22].

There have also been many experiments characterizing the adsorption of CO on single-crystalline Au in Ultra High Vacuum (UHV). As it is usually considered that Au(111) does not adsorb CO strongly, this surface is typically excluded from such studies, and the vast majority of UHV experiments involves CO adsorption on Au(110) or some other high-index atomically open gold surface. Early UHV measurements have shown that the heat of CO adsorption on Au(110) is weak (weaker than 33 kJ mol⁻¹/0.34 eV)

* Corresponding author at: Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands.

E-mail address: m.koper@chem.leidenuniv.nl (M.T.M. Koper).

[23]. Ruggiero et al. have reported an isosteric heat of CO adsorption of 55 kJ mol^{-1} (0.57 eV) on a Au(332) surface (at low coverage) employing a combination of low energy electron diffraction (LEED), thermal desorption spectroscopy (TDS) and reflection-adsorption infrared spectroscopy (RAIRS) [24]. Gottfried et al. reported a similar value of 59 kJ mol^{-1} (0.61 eV) (in the low-coverage limit) for the adsorption of CO on a reconstructed Au(110)-(1 × 2) under UHV conditions [25]. Weststrate et al. have shown that values of ca. 50 kJ mol^{-1} (0.52 eV) are typical binding energy values for CO adsorption on very open single-crystalline Au surfaces [26]. On the basis of FTIR spectroscopy, the atop binding geometry is found to be the most typical binding site for CO on single-crystalline gold in UHV [24,27].

There are also a number of publications studying the adsorption of CO on single-crystalline gold at elevated pressures. Such experiments have shown that CO may adsorb on Au(111) only at elevated pressures (>1 Torr), occupying the atop adsorption site [26]. Also, at such elevated pressures, adsorbed CO lifts the Au(111) herringbone reconstruction, with the initial CO adsorption taking place at steps and other low-coordinated Au sites [28–30]. Extensive reconstruction of the Au(110)-(1 × 2) surface has been observed at high CO pressures, with CO adsorbing atop [23,31].

Experiments do not solve all the questions about the atomic-level picture of CO adsorption on gold, which is why the theoretical or computational approach has become one of the most important tools for revealing details of the interactions occurring in CO–Au systems [32]. The DFT calculations available in the literature confirm the weak interaction of CO with Au(111) terraces, and also agree with the experimental observation that CO binds stronger to low-coordinated Au sites such as steps and kinks [33,34]. However, most computational studies conducted so far were based on neutral slabs, without any externally applied electric field, so that from the electrochemical point-of-view the current understanding of the potential-dependent CO adsorption on gold is incomplete.

The present paper presents a computational study of CO and OH adsorption on two low-index single crystalline gold surfaces, i.e. Au(111) and Au(110), using first-principles DFT calculations in the absence and presence of an electric field. We also studied how the binding energies of carbon monoxide and hydroxyl are influenced when they are co-adsorbed and their dependence on the binding geometry and gold surface structure, both in absence and presence of water. Our results may explain why only Au(111) shows a promoting effect for alcohol oxidation, whereas such an effect is not observed for Au(110) [17]. We note that some selected results presented herein were already published elsewhere [16,19], but we have included them for completeness' sake.

2. Computations

All calculations were carried out using the Vienna *ab initio* simulation package (VASP) [35,36]. Gold surfaces were represented by a supercell with an optimized lattice constant of $a = 4.174 \text{ \AA}$ containing six metal layers with adsorbates placed on only one side of the slab, and $\sim 14 \text{ \AA}$ of vacuum separating images of the metal slab. For structure optimization calculations of systems with a single adsorbate molecule, the (2 × 2) unit cell was used, whereas the CO–OH co-adsorption system was mainly studied in a (3 × 3) supercell. For some of the calculations of the Au(110) surface, a (2 × 3) unit cell was used.

The geometry search was performed using a cut-off for the plane-wave basis set of 400.00 eV. The Monkhorst–Pack scheme [37] with a $8 \times 8 \times 1$ and $6 \times 6 \times 1$ k-point sampling for (2 × 2) and (3 × 3) unit cells, resp., in the surface Brillouin zone was used to integrate the band energies. The Fermi level was smeared by the Methfessel–Paxton approach [38] with a Gaussian width of

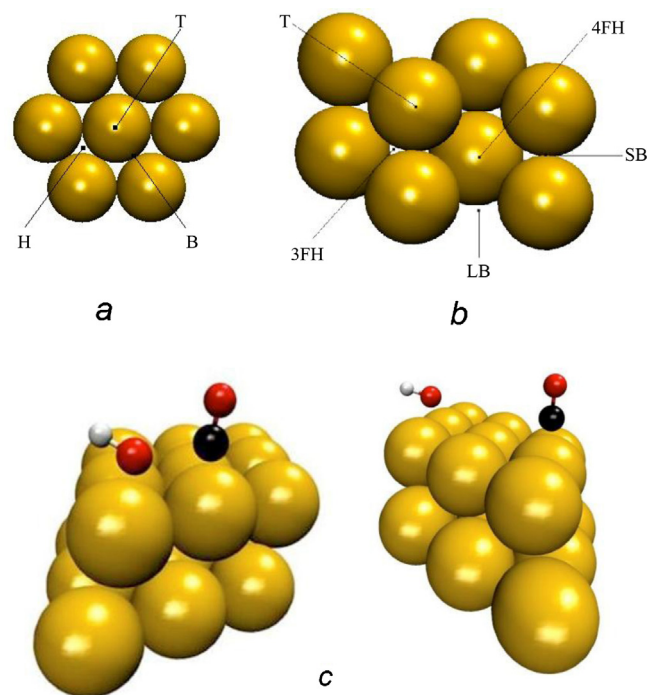


Fig. 1. Adsorption sites on the model: (a) (111) and (b) (110) surfaces; panel (c) illustrates two cases of CO and OH co-adsorption on Au(111).

0.2 eV. The free energy was extrapolated to zero Kelvin to yield total energies of the systems. During structure optimization calculations, the adsorbed molecules and two most outer metal layers were allowed to relax simultaneously with forces converged to $0.001 \text{ eV \AA}^{-1}$, while the four bottom layers were frozen to their bulk-like geometry. The Projector Augmented Wave core potentials [39] and Perdew–Burke–Ernzerhof (PBE) full electron frozen core approximation [40] to the exchange–correlation energy were used. The adsorption energy values were calculated from the following expression:

$$E_{ads} = E_{Au+CO(OH)} - (E_{Au} + E_{CO,g(OH,g)}) \quad (1)$$

here $E_{Au+CO(OH)}$ denotes the total energy of the gold surface with either CO or OH adsorbed on it, and E_{Au} and $E_{CO,g(OH,g)}$ correspond to the energy of the bare surface and the energy of the adsorbate in vacuum, respectively. The energy of the uncoordinated OH was calculated spin unrestricted; all surface calculations were done spin restricted, which generally works well for metal surfaces.

In calculations with zero electric field various adsorption sites have been considered: top (T), bridge (B) and tetrahedral threefold hollow (hcp) (H) for Au(111) (see Fig. 1a); top (T), short bridge (SB), long bridge (LB), threefold hollow (3FH) and fourfold hollow (4FH) for Au(110) (see Fig. 1b). Geometry optimizations for the adsorbate monomers have been performed for both surfaces for all adsorption sites in the (2 × 2) unit cell. CO and OH coverages were therefore $\Theta = 1/4 \text{ ML}$. For CO and OH co-adsorption on Au(111) a bigger (3 × 3) unit cell was utilized so that each adsorbate has a coverage $\Theta = 1/9 \text{ ML}$. The bigger unit cell has been used to study two general cases of CO–OH co-adsorption: nearest neighbor co-adsorption of CO and OH, and next-nearest neighbor co-adsorption of CO and OH on the surface, so that they are separated by a distance of $\sim 4.77 \text{ \AA}$ (Fig. 1c). Vibrational frequencies were obtained at the harmonic level with a numerical calculation and diagonalization of the force constant matrix by considering all the freedom degrees of the CO molecule on the surface.

Calculations with an electric field were performed using standard features provided within VASP. Unit cells with a single

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