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CO adsorption on Pd(111) at 0.5ML: A first principles study

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It is well-known experimentally that at ½ monolayer (ML) coverage CO forms a c(4×2) phase on Pd(111). There is, however, a debate about whether this adsorption is at the bridge or at the hollow (FCC and HCP) sites, or at a combination of these two types of sites. Using density functional theory based calculations to evaluate the structural and vibrational properties of the c(4 × 2) overlayer of CO on Pd(111), with all possible highly symmetric adsorption sites, we conclude that the CO molecules prefer to adsorb either only on the hollow (FCC or HCP) sites or only at sites which are located in-between the bridge and the FCC sites and that there is no stable overlayer structure in which the molecule binds only at the bridge sites or combination of bridge and hollow sites.

1. Introduction

CO adsorption on the Pd(111) surface is an interesting topic not only because of fundamental interest but also because Pd is widely used as an industrial catalyst. Despite extensive efforts in understanding the adsorption of CO on Pd(111) with almost all available surface science techniques [1–12] and state-of-the-art theoretical and computational methods [10,13–17], it is surprising that the overlayer structure at ½ monolayer (ML) coverage is still not well characterized, with contradictory information coming from different experimental and theoretical works. On the other hand, adsorption structures of CO on Pd(111) at low and high coverages are well understood. For example, there is agreement that for coverages less than ⅓ML, there is no ordered structure, rather CO molecules are found to adsorb on three-fold hollow (TFH) sites [2,18,19]. Between ⅓ML and ¾ML, however, several ordered structures have been reported [4]. At ⅓ML coverage, a $\left(\sqrt{3}\times\sqrt{3}\right)R30^\circ$ overlayer with CO molecules occupying FCC hollow sites is found [1]. This site assignment is not surprising, since at such low coverages the interaction between CO and the metal surface is the dominant factor that determines the binding site. At ¾ML coverage, however, intermolecular interactions become important and the overlayer structure assumes a (2 ×2) structure with (three) CO molecules adsorbed on the top and the FCC and HCP hollow sites. The above adsorption sites and overlayer structures of molecules have been confirmed experimentally [2] and with density functional theory (DFT) based calculations [2,13,20].

At ½ML coverage, interactions of CO molecules with both the metal surface and amongst themselves (intermolecular) become equally important which makes the understanding of the overlayer structure more complex and have led to contradictory interpretations by different research groups. Results from Low Energy Electron Diffraction (LEED) experiments [2,4] are in agreement that the structure is c(4×2)–2CO. However, there is no such consensus on the nature of the binding sites. Infra-Red Reflection-Absorption Spectroscopy (IRAS) measurements propose adsorption at the bridge sites (Bridge-Bridge) [2,3,5], while photoelectron diffraction [6], High Resolution X-ray Photoelectron Spectroscopy (HR-XPS) and High Resolution Electron Energy Loss Spectroscopy (HR-EELS) [7] point to the involvement of only FCC and HCP (FCC-HCP) hollow sites [6,7]. At the same time, Scanning Tunneling Microscopy (STM) study of Rose et al. [9] showed the coexistence of two islands at ½ML CO coverage on Pd(111) in which binding sites assignment for each island, based on the appearance of protrusions, concluded simultaneous presence of both Bridge-Bridge and FCC-HCP occupancies. On the other hand, High Resolution Core Level Shift Spectroscopy (HRCLS) combined with DFT based calculations by Martin et al. [10] concluded that at this coverage the CO molecules adsorb on a mixture of FCC-Bridge and HCP-Bridge sites.

The question thus remains: is the bridge site involved in the c(4 ×2)–2CO structure on Pd(111)? We address this question by carrying out first principles calculations based on DFT of the overlayer structure of CO on the Pd(111) surface at ½ML coverage. We show that indeed two possible combinations of adsorption sites exist: the first consists of CO molecules adsorbed on equal mixture of FCC and HCP hollow sites (FCC-HCP) and the second consists of CO molecules adsorbed on sites located between the

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FCC hollow and the bridge sites (FCC-Bridge Hybrid).

The paper is organized as follows: In the next section, calculational details are provided. In Section 3 we discuss the results from this study in view of those from previous experimental and theoretical results.

2. Calculation method

The calculations in this study include those of the system total energy, adsorbate vibrational frequencies, and simulation of STM images. Some details for each are given below.

2.1. Total energy calculations

We performed DFT [21,22] calculations employing the projector-augmented wave (PAW) [23,24], plane-wave basis set, and the supercell method as implemented in the Vienna Ab-initio Simulation Package (VASP) [25]. We described the exchange-correlation interaction of electrons by the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhoff (PBE) functional [26]. We set the cutoff for kinetic energy of plane-wave expansion at 500 eV. Our supercell consists of a five-layer Pd(111) slab constructed with optimized lattice parameter of 3.94 Å, with CO molecules adsorbed on one side of the slab and a vacuum of 20 Å to separate the slab and its normal periodic images. We sampled the Brillouin zone with a uniform $18 \times 18 \times 18$ and $9 \times 11 \times 1$ mesh centered at the zone center corresponding to a unit cell of bulk Pd and the Pd(111) surface (see Fig. 1), respectively. We relaxed all structures until all components of the force acting on each atom were smaller than 0.001 eV/Å.

To estimate the role of van der Waals (vdW) interactions in determining the adsorption sites at ½ML coverage, calculations were also performed by using the optB88-vdW [27] functional. For testing purpose, some of the calculations were repeated with PW91 [28] functional as well.

For all optimized structures (obtained after ionic-relaxation) the binding energy (BE) is calculated by $BE = E_{slab+adsorbate} - E_{slab} - 2 \times E_{adsorbate}$, in which $E_{slab+adsorbate}$ is the total energy of the system consisting of the Pd(111) slab and CO, E_{slab} represents the total energy of the clean Pd(111) slab and $E_{adsorbate}$ gives the total energy of the CO molecule in gas phase. The binding energies are then averaged over the number of CO molecules in the unit cell.

2.2. Calculations of vibrational frequencies

We calculated vibrational frequencies of the system by using the finite difference method in which atoms are displaced by 0.01 Å along each direction of the three Cartesian coordinates. The forces on the atoms so generated are calculated using Hellmann-Feynman theorem. From the obtained forces, the Hessian matrix was constructed and diagonalized using the Phonopy code [29]. A scaling factor of 1.0216 was applied to obtain frequencies so that the calculated C-O stretch frequency, using PBE, in gas phase equals the experimental value of 2170 cm^{-1} [30] (scaling factors of 1.0191 and 1.0084 were used for frequencies obtained by PW91 and optB88-vdW functionals, respectively).

2.3. Simulation of STM images

We simulated STM images [31] by using the Tersoff and Hamann [32,33] method, i.e. the tunneling current at low voltage is assumed to be proportional to the local density of states (LDOS) around the Fermi level at the position of the tip apex. In our calculations, the topological STM image is approximated to be the LDOS isosurface with value of 10^{-6} e/ Å^3 contributed from all states in the energy range of −0.1 eV to 0.00 eV (i.e. within 0.1 eV of the Fermi level).

3. Results and discussions

3.1. Testing the reliability of DFT functional

Previous body of work [34–41] suggests that DFT does not always predict correctly the adsorption site for CO on close-packed transition metal surfaces. We tested the case of ⅓ML coverage of CO on Pd(111) because we are aware from experiments that at this

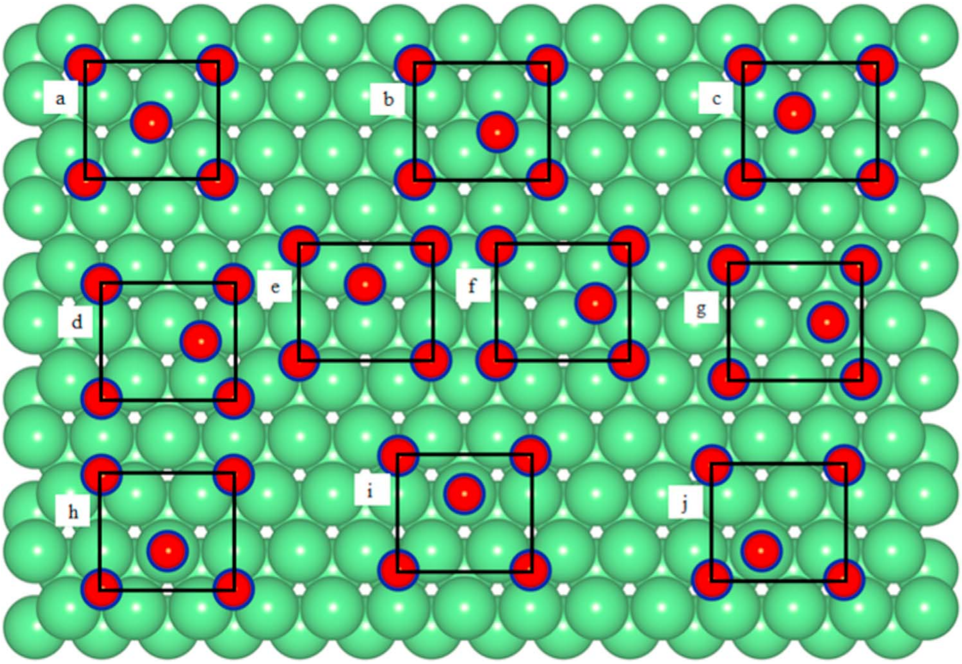

Fig. 1. Considered binding sites at ½ML forming c(4 × 2)–2CO structure as listed in Table 1. Each rectangle represents a c(4 × 2)–2CO surface unit cell. The notations a-j are described in Table 1.